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**Characterization and Graphical Visualization of Fluxes of Oxides of Nitrogen from  
Agricultural Soils in North Carolina**

by

**Captain Benny Daryl Holbrook**

**United States Air Force**

**North Carolina State University  
Degree of Master of Science**

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## ABSTRACT

Oxides of nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) play a central role in tropospheric photochemistry. Natural biogenic emissions of  $\text{NO}_x$  from soils are usually considered to be only a small fraction of the anthropogenic emissions, but the source strength is not well known. Field measurements of  $\text{NO}_x$  were made in two seasons (summer and winter) in an agriculturally-managed field in North Carolina. The NO flux estimates were used to produce a graphical representation of the spatial distribution of ozone precursors in the state, and to assess the magnitude of these biogenic soil NO emissions as a percentage of the total NO emissions in the state.

A significant negative correlation between NO flux and ambient  $\text{O}_3$  concentration, supports the hypothesis that soil emissions of NO contribute to local production of  $\text{O}_3$  in rural areas. The winter measurements suggest that significant fluxes are generated during fallow periods when the plant residue is mixed back into the soil, a common agricultural practice.

Using the assumption that the calculated NO fluxes are representative of those across North Carolina, these fluxes were used to develop graphical displays of the spatial distribution of soil NO emissions in the state, with a county spatial resolution. These NO emission estimates were compared to other values in the literature. Estimates of the soil emission of NO as a percentage of total (all sources) NO emission in the state were compared to the current input values used in the Regional Oxidants Model (ROM). The values calculated from these measurements are significantly larger than those currently used in the ROM.

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## ABSTRACT

HOLBROOK, BENNY DARYL. Characterization and Graphical Visualization of Fluxes of Oxides of Nitrogen from Agricultural Soils in North Carolina. (Under the direction of Viney P. Aneja and Vinod K. Saxena.)

Oxides of nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) play a central role in tropospheric photochemistry. In terms of global source strength,  $\text{NO}_x$  sources are dominated by anthropogenic emissions from the burning of fossil fuels or from biomass burning. Natural biogenic emissions from soils are usually considered to be only a small fraction of the anthropogenic emissions, but the source strength is not well known. Field measurements of  $\text{NO}_x$  were made in two seasons in an agriculturally-managed field. The NO flux estimates were used to produce a graphical representation of the spatial distribution of ozone in the state, and to assess the magnitude of these biogenic soil NO emissions as a percentage of the total NO emissions in the state.

It is presently recognized that both nitrifying bacteria in aerobic environments and denitrifying bacteria in anaerobic environments produce NO. Field studies of NO emission rates show that they are a function of soil type, soil temperature, soil moisture content, past use (fertilization or domestic animal grazing), vegetation cover, season, surface wind speed, specific location within seemingly uniform areas, and NO (and perhaps  $\text{NO}_2$ ) levels in the air above the soil. To date, three general techniques have been used for most of the published measurements of  $\text{NO}_x$ : the chamber technique, the gradient technique, and the eddy correlation technique.

Agricultural soil NO flux measurements were made from August 18 to September 1, 1993 in the Upper Coastal Plain region of North Carolina in an effort to

determine the potential role of natural emissions of NO on the formation of ozone in rural areas (Section I). Overall average NO flux rates increased proportionally to the level of applied fertilizer nitrogen in the agricultural soil. The soybean, cotton and corn field measurements revealed an average NO flux of 1.79 (range -1.0 to 6.9)  $\text{ng-N m}^{-2} \text{s}^{-1}$ ; 3.77 (range -0.1 to 38.0)  $\text{ng-N m}^{-2} \text{s}^{-1}$ ; and 8.05 (range -0.5 to 52.8)  $\text{ng-N m}^{-2} \text{s}^{-1}$  respectively. There was a positive correlation between NO concentration near the soil surface (~50 cm) and NO flux. A significant negative correlation between NO flux and ambient  $\text{O}_3$  concentration, however, supports the hypothesis that soil emissions of NO contribute to local production of  $\text{O}_3$  in rural areas.

The fluxes of NO and  $\text{NO}_2$  from a fallow field to the atmosphere were measured (Section II). Two identical chambers were used, with ambient air as the carrier gas in one, and nitrogen as the carrier gas in the other. Overall average NO flux rates increased proportionally to carbon/nitrogen ratio of the plant residue plowed back into the soil at the end of the previous growing season. The soybean, cotton and corn field measurements revealed an average NO flux of 10.23 (range -10.77 to 133.06)  $\text{ng-N m}^{-2} \text{s}^{-1}$ ; 5.07 (range -11.71 to 109.55)  $\text{ng-N m}^{-2} \text{s}^{-1}$ ; and 3.68 (range -17.51 to 40.39)  $\text{ng-N m}^{-2} \text{s}^{-1}$  respectively, using the ambient air carrier gas. The winter measurements suggest that significant fluxes are generated during fallow periods when the plant residue is mixed back into the soil, a common agricultural practice.

Using the assumption that the NO fluxes described in the preceding two sections are representative of those across North Carolina, these fluxes were used to develop graphical displays of the spatial distribution of soil NO emissions in the state.

(Section III). The visualizations have a county spatial resolution. Visualizations were developed for each crop type, during both measurement periods, using the ambient air based NO flux values. These NO emission estimates were compared to other values in the literature, (normalized to NC crop acreage). Estimates of the soil emission of NO as a percentage of total (all sources) NO emission in the state were compared to the current input values used in the Regional Oxidants Model.

**Characterization and Graphical Visualization of Fluxes of Oxides of Nitrogen from  
Agricultural Soils in North Carolina**

by

**Benny Daryl Holbrook**

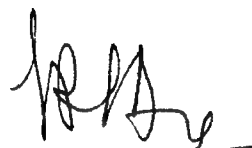
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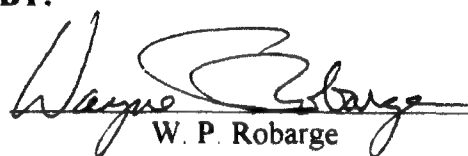
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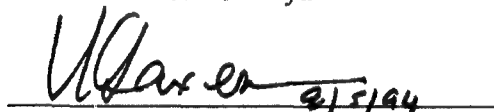
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## SECTION I: MEASUREMENTS OF NITROGEN OXIDE FLUX FROM AN UPPER COASTAL PLAIN, NORTH CAROLINA AGRICULTURAL SOIL

### Abstract

Agricultural soil  $\text{NO}_x$  flux measurements (using a dynamic chamber technique) were made from August 18 to September 1, 1993 in the Upper Coastal Plain region of North Carolina in an effort to determine the role of natural emissions of NO on rural atmospheric photochemistry. Overall average NO flux rates increased proportionally to the level of applied fertilizer nitrogen in the agricultural soil. The soybean, cotton and corn field measurements revealed an average NO flux of 1.79 (range -1.0 to 6.9)  $\text{ng-N m}^{-2} \text{s}^{-1}$ ; 3.77 (range -0.1 to 38.0)  $\text{ng-N m}^{-2} \text{s}^{-1}$ ; and 8.05 (range -0.5 to 52.8)  $\text{ng-N m}^{-2} \text{s}^{-1}$  respectively. There was a positive correlation between NO concentration near the soil surface (~50 cm) and NO flux. A significant negative correlation between NO flux and ambient  $\text{O}_3$  concentration, however, supports the hypothesis that soil emissions of NO contribute to local production of  $\text{O}_3$  in rural areas.

## INTRODUCTION

Gaseous oxides of nitrogen ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ) are trace atmospheric constituents that function directly or indirectly as potentially important greenhouse gases in various global climate change scenarios (Duxbury et al., 1993).  $\text{NO}_x$  also participates in the production and/or consumption of atmospheric oxidants (e.g.  $\text{O}_3$ ,  $\text{OH}$ ) and is removed from the atmosphere in a series of photochemical reactions that result in formation of  $\text{HNO}_3$  (Logan, 1983). In addition, it has been suggested that  $\text{NO}_x$  emissions from soils may comprise a significant fraction of the unaccounted losses observed in the nitrogen budget of fertilized agricultural soils (Hutchinson and Davidson, 1993).

Measurements of  $\text{NO}_x$  emission at a variety of locations around the globe (Slemr and Seiler, 1984; Anderson and Levine, 1987; Williams et al. 1987, 1988; Johansson et al., 1988; Johansson and Sanhueza, 1988; Johansson and Granat, 1984; Kaplan et al., 1988; Williams and Fehsenfeld, 1991; Hutchinson and Brams, 1992; Valente and Thornton, 1993; Kim et al., 1994) have shown that soil emissions are highly variable both temporally and spatially, and this variation can be substantial. The high variability is due to variations in soil physical, chemical and biological parameters including soil temperature, soil water content, past use (fertilization or domestic animal grazing), vegetation cover, season, surface wind speed, and  $\text{NO}$  (and possibly  $\text{NO}_2$ ) levels in the air above the soil (Williams et al., 1987; Kim et al. 1994).

Because biogenic emissions from microbial processes in soil are thought to be one of the principal sources of atmospheric nitrogen oxides, it becomes important to determine the magnitude of this source and, if appropriate, to develop control technologies, such as alternative soil management practices, or improved fertilizer formulations and application techniques (Hutchinson and Brams, 1992). Uncertainties in

NO<sub>x</sub> budgets could cause an incorrect assessment of the role of biogenic NO<sub>x</sub> in atmospheric chemistry. It has been suggested that NO<sub>x</sub> emission from soils in rural areas may represent a more significant source of NO<sub>x</sub> than was initially estimated (Williams et al., 1988). Since NO<sub>x</sub> emissions data is used as input for photochemical models, representative estimates of biogenic flux are critical for regional photochemical modeling studies (Kim et al., 1993).

Without an accurate assessment of the magnitude of NO<sub>x</sub> emissions from soil, and its inclusion into air quality models, the effectiveness of subsequent ozone control strategies is diminished. This paper presents preliminary results of the measurement of NO<sub>x</sub> emissions from agriculturally-managed soils in the Upper Coastal Plain of North Carolina. These measurements were taken in three different agriculturally-managed fields, each containing a crop representing a different level of applied fertilizer nitrogen. The measurements were made using a dynamic chamber technique (Aneja, 1975; Hill et al., 1978; Aneja et al., 1979) in order to gain insight into the role of natural emissions of NO<sub>x</sub> on rural photochemistry. Observations of ambient O<sub>3</sub> complement these measurements.

These emission estimates will also be used to show the spatial distribution of NO fluxes in North Carolina, and will be compared to the current input values used in the Regional Oxidants Model (ROM), to assess the validity of the current input values.

## EMISSION ESTIMATES

In terms of global source strength, NO<sub>x</sub> sources are dominated by anthropogenic emissions from the burning of fossil fuels or from biomass burning (Logan, 1983; Anderson et al., 1988). These sources are generally located in highly industrialized or

densely populated regions. Natural  $\text{NO}_x$  sources include microbial processes in soil, lightning, oxidation of atmospheric  $\text{NH}_3$ , photolytic and biological processes in the ocean, and stratospheric injection (Warneck, 1988). Natural biogenic emissions from soils are usually considered to be only a small fraction of the anthropogenic emissions, but the source strength is not well known (Anderson and Levine, 1987).

Globally, sources of atmospheric  $\text{NO}_x$  are about equally distributed between anthropogenic ( $\sim 30 \text{ Tg N yr}^{-1}$ ) and natural ( $\sim 20 \text{ Tg N yr}^{-1}$ ) (Watson et al. (1992). However, Hutchinson (1993) suggests that the soil source of NO alone may represent as much as 40% of the global  $\text{NO}_x$  budget. Given the measured variability (both temporal and spatial) and experimental uncertainties, estimation of global or regional source magnitudes of soil  $\text{NO}_x$  emission is very uncertain.

Global estimates of soil emitted NO range from  $1 \text{ Tg N yr}^{-1}$  (Johansson, 1984) to  $11 \text{ Tg N yr}^{-1}$  (Slemr and Seiler, 1984) to  $15 \text{ Tg N yr}^{-1}$  (Lipschultz et al., 1981) to  $20 \text{ Tg N yr}^{-1}$  (Davidson, 1991). The coefficient of variation in measured  $\text{NO}_x$  emissions is typically 100% or greater, even in locations which are characterized as homogeneous (Valente and Thornton, 1993).

## PRODUCTION MECHANISMS

Nitrogen enters the biosphere largely by way of bacterial nitrogen fixation. The term fixed nitrogen is used to describe nitrogen contained in chemical compounds that all plants and microorganisms can utilize. Figure 1 serves as a guide for the biochemical transformations of the various compounds representing fixed nitrogen. Dead organic matter undergoes decomposition by a host of different bacteria. Thereby, organic nitrogen is mineralized to ammonium unless it is assimilated. Under aerobic conditions, a



number of specialized bacteria derive their energy needs from the oxidation of ammonium to nitrite and then further to nitrate. This process is called nitrification (Warneck, 1988). Nitrate is the major end product of nitrification. Most plants can utilize nitrate as well as ammonium to satisfy their nitrogen needs. A fraction of this nitrate, however, undergoes bacterial reductions toward  $N_2$  (Warneck, 1988). This process is called denitrification.

It is presently recognized that both nitrifying bacteria in aerobic environments and denitrifying bacteria in anaerobic environments produce NO. Lipschultz et al. (1981) found NO and/or  $NO_2$  as direct products of nitrification, evolving concurrently with nitrite (Figure 2). Focht and Verstraete (1977) identified NO as an intermediate species in denitrification.

## Nitrification

Nitrification is defined as the biological oxidation of ammonium ( $NH_4^+$ ) to nitrite ( $NO_2^-$ ) and nitrate ( $NO_3^-$ ), or a biologically induced increase in the oxidation state of N (Soil Science Society of America, 1987). Numerous studies have indicated that nitrification is a quantitatively important part of the N cycle in most cultivated agricultural soils (Hutchinson and Davidson, 1993).

The process of nitrification is associated with the metabolism of chemoautotrophic bacteria of the family *Nitrobacteriaceae*, with the preponderance of nitrification in soil accomplished by a few genera - *Nitrosomonas* and *Nitrospira*, which oxidize  $NH_4^+$  to  $NO_2^-$ , and *Nitrobacter*, which converts  $NO_2^-$  to  $NO_3^-$  (Hutchinson and Davidson, 1993).

The biochemical pathway of chemoautotrophic nitrification remains the subject of much debate. There is good evidence that hydroxylamine ( $NH_2OH$ , N oxidation state -1) is the first intermediate product of  $NH_4^+$  oxidation (Figure 1), but subsequent

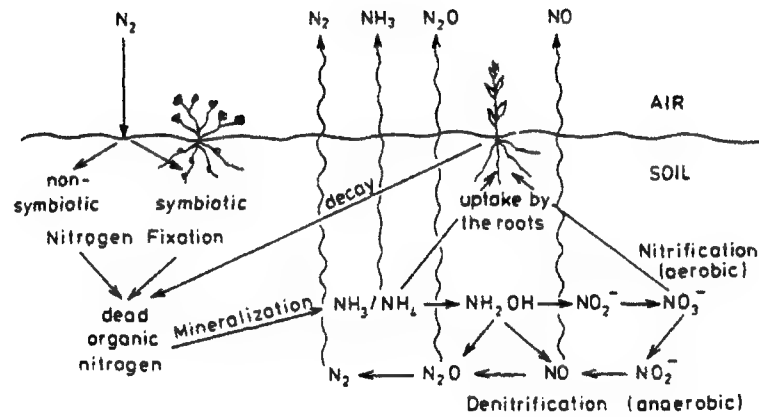


Figure 1. The biological nitrogen cycle in the atmosphere-soil system. (Warneck, 1988)

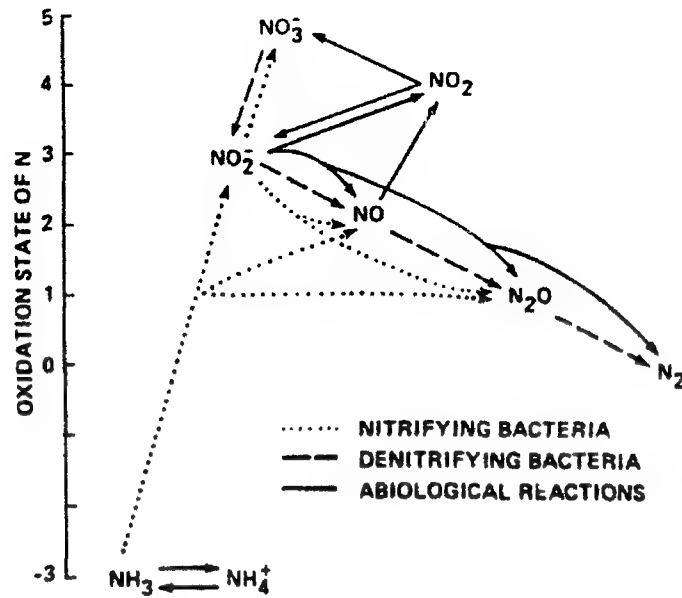


Figure 2. Biological and abiological processes of production and consumption of  $NO$ . (Davidson, 1991)

intermediates with N oxidation states +1 and +2 are not known with any certainty (Hooper, 1984). The oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  by *Nitrobacter* is a simple two-electron shift in N oxidation state from +3 to +5 (Figure 2) and involves no intermediates (Schmidt, 1982).

There is abundant evidence that NO is included among the products of chemoautotrophic nitrification. It has long been known that NO is produced by chemoautotrophic nitrifiers in culture, but only much more recently recognized that this process serves as a significant source of NO emitted from soil (Hutchinson and Davidson, 1993). Studies using acetylene or nitrapyrin to inhibit  $\text{NH}_4^+$  oxidation and chlorate to inhibit  $\text{NO}_2^-$  oxidation have shown that NO produced during chemoautotrophic nitrification are a direct result of the activity of those organisms responsible for the first step of this process, i.e., oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  (Davidson, 1992; Tortoso and Hutchinson, 1990).

### Denitrification

Denitrification is defined as respiratory reduction of  $\text{NO}_3^-$  or  $\text{NO}_2^-$  to gaseous NO,  $\text{N}_2\text{O}$  or  $\text{N}_2$  (Figure 1) that is coupled to electron transport phosphorylation (Hutchinson and Davidson, 1993). Denitrification occupies a position of pivotal importance in the N cycle of the biosphere. In its absence, all biologically available N that has been released from igneous rocks of the Earth's original crust and mantle would have been converted long ago to its more thermodynamically stable form of  $\text{NO}_3^-$  in the oceans (Lindsay et al., 1981).

Unlike the narrow species diversity of organisms responsible for nitrification in soil, denitrification capacity is common to several taxonomically and physiologically

different bacterial groups (Hutchinson and Davidson, 1993). Included among the denitrifiers are phototrophs, lithotrophs, and organotrophs that derive energy for growth and regeneration from light, inorganic substrates, and organic substrates, respectively (Hutchinson and Davidson, 1993). The latter group dominates the denitrifying populations of natural soil and water environments. Within this group species of *Pseudomonas* predominate, and except in special or unusual environments most of the remaining denitrifying organisms are species of the closely related *Alcaligenes* (Tiedje, 1988).

NO is not usually considered to be a major end product of denitrification in soil. Although this belief may partially reflect that convenient and sensitive methodology for NO analysis has only been available for the last decade, mass balance experiments long ago confirmed the absence of a major unknown denitrification product (Hutchinson and Davidson, 1993). Nevertheless, Tortoso et al. (1986) reported that NO was the principal denitrification product when they initiated the process in laboratory-incubated soil by removing O<sub>2</sub> from the air stream sweeping the incubation jar headspace. In the natural soil environment denitrification generally occurs only when the soil's water content is high enough to restrict O<sub>2</sub> availability, which also restricts the diffusion rates of other gases in soil (Baumgartner et al., 1992). The resulting increase in time required for NO diffusion to the soil surface, combined with its instability toward further reduction, allows very little NO to escape (Hutchinson and Davidson, 1993).

## ENVIRONMENTAL CONTROLS ON SOIL NO<sub>x</sub> EXCHANGE

Despite increasing understanding of cellular level controls on the microbial production and consumption of gaseous oxides of nitrogen, applying that knowledge to

explain and predict variation in soil NO across and within landscapes, or even in small plot studies, remains troublesome (Hutchinson and Davidson, 1993). However, despite the large variability of soil NO<sub>x</sub> exchange rates (Williams et al., 1992) and the diversity of processes involved in the production, consumption and transport of these N gases, various patterns are obvious when field-measured exchange rates are analyzed. For example, warm, relatively dry soils produce more NO than wet cool soils, so grasslands and savannah soils tend to be stronger sources than forest soils at the same latitude (Hutchinson, 1993). Johansson et al. (1988) observed larger average NO emission from savannah areas than forested areas in Venezuela. They also reported that the NO fluxes measured from both areas were from 3 to 30 times larger than from analogous ecosystems in temperate regions. Field studies of NO emission rates (Johansson, 1984; Johansson and Granat, 1984; Slemr and Seiler, 1984; Shepherd et al., 1991; Kim et al., 1994) show that they are a function of soil type, soil temperature, soil moisture content, past use (fertilization or domestic animal grazing), vegetation cover, season, surface wind speed, specific location within seemingly uniform areas, and NO (and perhaps NO<sub>2</sub>) levels in the air above the soil. Of these various parameters, soil temperature, moisture content and available N appear to exert the dominant influence on NO flux from soils.

### Soil Temperature

The relationship between NO emission rate and soil temperature most often reported in the literature (Williams et al., 1992; Valente and Thornton, 1993; Kim et al., 1994, and references therein) is exponential, of the form

$$\text{NO emission rate} = A \exp^{BT} \quad (1)$$

where the emission rate is expressed in units of  $\text{ng N m}^{-2} \text{ s}^{-1}$ ,  $T$  is the 5 cm soil temperature in degrees Celsius, and  $A$  and  $B$  are fitted parameters with  $A$  reflecting soil land use category. This formula has been shown to hold for temperatures ranging from  $15^\circ$  to  $35^\circ\text{C}$  (Williams and Fehsenfeld, 1991) with emission nearly doubling for each  $10^\circ\text{C}$  increase in temperature. Additionally, while the optimum temperature for denitrification may vary from one area to another, the rate of denitrification also increases by approximately a factor of 2 for every  $10^\circ\text{C}$  increase in temperature (Haynes and Sherlock, 1986). Changes in temperature below about  $15^\circ\text{C}$  typically have much greater effect on the rates of all biological processes than changes above this threshold and are not well characterized by equation (1) (Ingraham, 1962). However, the potential for important soil emission of  $\text{NO}$  at low temperature cannot be discounted because the organisms responsible for both nitrification and denitrification are known to possess the capacity for adaptation to extreme climates (Focht and Verstraete, 1977; Haynes and Sherlock, 1986).  $\text{NO}$  emission from soil also decreases at temperatures in excess of about  $35^\circ\text{C}$ . Intuitively, biogenic activity will eventually reach a maximum with increasing temperature, with the location of this maximum with increasing soil temperature confounded by soil moisture and available nutrients (Williams and Fehsenfeld, 1991; Aneja et al., 1994).

### Soil Moisture

Although nitric oxide emissions follow changes in soil temperature, this correlation is complicated by the dependence of  $\text{NO}$  emission on soil moisture content. Soil moisture content affects  $\text{NO}_x$  production, consumption and transport, with the most

important effect (outside its universal requirement by all life processes) resulting from its strong influence on both gas phase and solution phase diffusive transport rates (Hutchinson, 1993). Higher water contents increase the ratio of water-filled to air-filled pore space, resulting in thicker water films lining the remaining air-filled pores, thus enhancing the transport of species in solution, while retarding that of gases in the soil atmosphere. This suggests that for aerobic microbial processes like nitrification, the overall process rate is probably limited by solution-phase substrate diffusion through the water films in dry soil, and by gas-phase  $O_2$  diffusion in wet soil (Hutchinson, 1993). The optimum soil water content for aerobic processes is about 60% water-filled pore space (%WFPS, Figure 3) (Linn and Doran, 1984), but it is important to realize this value applies to overall process rates, rather than the production of specific end products (Davidson, 1993). In addition to these transport-related effects of soil water content on  $NO$  evolution rate, several authors have reported a large burst of emissions following wetting of a very dry soil (e.g., Slemr and Seiler, 1984; Anderson and Levine, 1987; Williams et al., 1987; Davidson, 1992). Emission rates during such an event can be up to three orders of magnitude higher than preceding or following rates, so that the quantity of soil N lost during its short duration may exceed the total amount emitted during the relatively long periods between times that the soil dries and the next addition of water (Hutchinson, 1993).

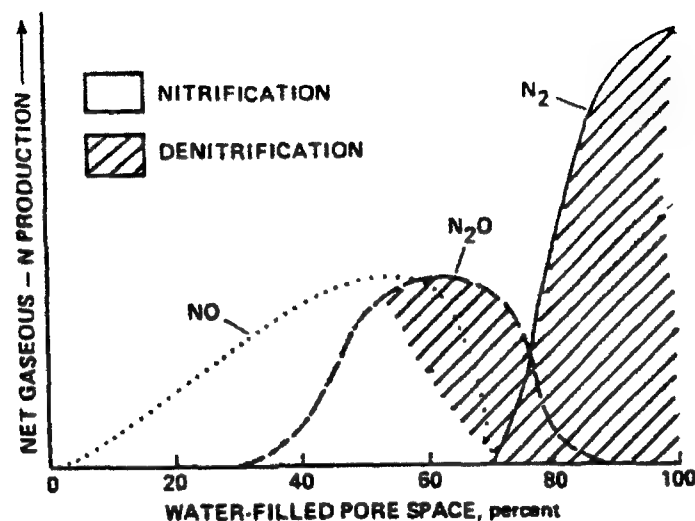


Figure 3. Model of the relationship between WFPS (water-filled pore space) of soil and relative fluxes of N gases. (Davidson, 1991)

Interestingly, subsequent wettings by irrigation or rainfall may produce further significant increases in emissions above the levels measured from dry soils, but the amount is small compared to that observed for a single wetting of a very dry soil (Johansson et al., 1988; Williams et al., 1987). Reasons for this unusually large response of N oxide emissions to wetting of dry soil remain unclear.

#### Soil Nitrogen Availability

There is abundant evidence that the availability of organic and inorganic N in soils also strongly influences NO emission (Slemr and Seiler, 1984; Anderson and Levine, 1987; Williams et al., 1987; Davidson, 1992; Hutchinson and Brams, 1992; Hutchinson, 1993). Because both nitrification and denitrification are often substrate limited, soil  $\text{NH}_4^+$  or soil  $\text{NO}_3^-$  pool sizes might be expected to serve as useful indicators of the rate of N transformation, and thus to forecast NO exchange rates (Firestone and Davidson, 1989). However, because the turnover rates of soil inorganic N pools are sometimes very rapid,



pool sizes may not accurately reflect the prevailing rate of N cycling, or, more specifically, the rate of substrate supply to nitrifying or denitrifying bacteria (Hutchinson, 1993). For example, Davidson et al. (1990) estimated that turnover time of the soil  $\text{NH}_4^+$  pool in a dry California grassland was about one day, so low measured  $\text{NH}_4^+$  concentrations were a poor indicator of the rate of  $\text{NH}_4^+$  supply.

Unfortunately, all reported correlations tend to be site-specific or study-specific, and no single predictive parameter (or combination of parameters) has emerged that accurately reflects the effect of soil NO emissions across all sites and studies (Davidson, 1991). Failure to find common predictors probably reflects that (1) two very different processes are involved, i.e., nitrification and denitrification, (2) other process-limiting factors that interact with N availability may be more important at some sites than others, and (3) the scale chosen for investigation influences the nature of the predictors likely to be found useful (Hutchinson, 1993). For example, soil  $\text{NO}_3^-$  concentration was a good predictor of NO emissions when hardwood forests were compared to fertilized corn fields, but it did not account for substantial variation within each location (Williams and Fehsenfeld, 1991); at the latter scale, modest topographic gradients or local scale effects of crop residues may be important contributors to the observed variability. It is not clear whether the relation of NO emissions to soil  $\text{NO}_3^-$  concentration at the larger scale reflects the importance of this ion as a substrate for denitrification, as a product of nitrification, or simply that  $\text{NO}_3^-$  tends to accumulate in soils where N is abundant compared to the availability of readily-oxidizable carbon (Hutchinson, 1993).

## MEASUREMENT TECHNIQUES

To date, two general classes of techniques have been used for most of the published measurements of  $\text{NO}_x$ : chamber techniques, and meteorological techniques, which encompasses the gradient technique and the eddy correlation technique

### Chamber Technique

The chamber technique can be subdivided into two different types: the static chamber and the dynamic chamber methods.

The static chamber is sealed to the atmosphere, and has a relatively large volume in comparison to the size of the sample taken, with the sample volume typically  $\sim 1\%$  of the chamber volume. Most static chamber designs in the literature have internal stirring fans to ensure well-mixed conditions exist throughout the chamber. Valente and Thornton (1993) compared measured concentrations of NO within their sealed chamber with and without replacement of the withdrawn sample air ( $\sim 1.5\%$  of the chamber volume) by an equal amount of purified (zero) air. Their results showed no significant difference between replacement and no replacement, even after five samples were drawn ( $\sim 7.5\%$  of the chamber volume). This result will vary with chamber volume and sample flow rate.

In the dynamic chamber technique, a carrier gas (normally ambient air, zero air, or nitrogen, ( $\text{N}_2$ )) is passed through the chamber. The  $\text{NO}_x$  concentration at the chamber output (along with the chamber input  $\text{NO}_x$  concentration when ambient air is used as the carrier gas) is used to determine the soil emission of  $\text{NO}_x$ . Additional quantities needed are soil and air temperature, flow rate through the chamber, chamber volume, cross-sectional area, and losses in the chamber, which are all relatively easy to characterize.

Typically, the chamber volumes range from ~ 25 liter (dynamic) to ~ 100 liter (static), and are lined with Teflon film to minimize wall loss of the measured species. The chambers are normally placed on a frame placed 2-10 cm into the soil. Measurements are normally delayed a few hours (or days) to minimize the effects of possible disruption of the soil environment on  $\text{NO}_x$  emission. Flow rates in dynamic chambers range from sub-liter to tens of liters per minute. Deliberate leaks are often used to minimize the pressure differences between the atmosphere and the chamber in dynamic chambers. Both opaque and transparent chambers have been utilized.

Chamber techniques are extensively used for  $\text{NO}_x$  measurements, due to their portability, ease of use, low manpower requirements, relatively low cost when compared to other techniques, placement flexibility, and quick sampling time. Drawbacks include the neglect of vegetation uptake effects due to the small chamber volume, and the inherent assumption of soil homogeneity. However, Parrish et al. (1987) found this effect was negligible when compared to the measured variability of the emission of NO from soils.

### **Micrometeorological Techniques**

Gradient Technique. The gradient technique is based on measurements of NO and  $\text{O}_3$  at different heights above the soil (Parrish et al, 1987). A vertical gradient is established in the mixing ratio of NO because it is emitted at the surface and is then mixed upward in the atmosphere. In the atmosphere NO reacts rapidly with the  $\text{O}_3$  to produce  $\text{NO}_2$ . The atmospheric concentration of ozone is several orders of magnitude larger than that of NO at night in relatively unpolluted air masses. During the nighttime hours, the vertical gradient of NO concentration is determined solely by the rates at which NO is emitted

from the soil, mixed upward by near surface atmospheric transport and diffusion processes, and destroyed by reaction with ozone (Parrish et al., 1987). It is assumed that NO emitted from the soil equals the integrated loss in the lowest layer of the atmosphere above the surface due to the reaction with ozone (Johansson and Sanhueza, 1988); i.e.,

$$\text{NO emission} = \int_{z=0}^{\infty} k[\text{NO}][\text{O}_3]dz \quad (2)$$

where  $k$  is the rate constant for the reaction between  $\text{O}_3$  and NO (DeMore et al., 1985), brackets  $[\ ]$  denote concentrations of the species, and  $z$  is the height above the surface. To evaluate this integral fully, profiles of  $[\text{NO}]$  and  $[\text{O}_3]$  (and even temperature, since  $k$  depends on temperature) must be known, while the measurements give only two or three points near the surface. However, these points are in the atmospheric layer that makes the major contribution to the integral. Thus a good approximation of NO emission may be obtained from an approximate integration (Parrish et al., 1987).

To effect the integration, an approximate analytical solution is fit to the measurements of NO concentration. Therefore, several approximations are necessary; (1) the transport of NO can be adequately described by considering only vertical turbulent diffusion; i.e., the transport can be parameterized with a single eddy diffusion coefficient,  $K$ , which implies an isotropic horizontal NO distribution (Parrish et al., 1987); (2) the ozone mixing ratio and temperature are taken to be constant with height, and (3)  $K$  is assumed to increase linearly with altitude (Jacobi and Andre', 1963). Parrish et al. (1987) assessed the validity of these assumptions, and concluded that (a) this method is valid as long as the measurements span the height interval that gives the major contribution to the interval, and (b) the emission rate magnitudes change by less than

30% over a variety of different assumptions concerning the form used to describe the vertical variation of the eddy diffusivity.

During the daytime, the reconversion of  $\text{NO}_2$  to  $\text{NO}$  by sunlight provides an additional source of  $\text{NO}$  which is distributed vertically according to the gradient of the concentration of  $\text{NO}_2$ . Therefore, the gradient method for measuring  $\text{NO}$  emissions is normally only applied to nighttime periods. Additionally, the need for simultaneous measurements of  $\text{NO}$  and  $\text{O}_3$  concentrations at several levels make the determination of  $\text{NO}$  emissions more unwieldy and more costly than the chamber method.

#### Eddy Correlation Technique.

The mass flux, or more precisely, the mass flux density,  $F_C$  of a substance of concentration  $c$  is calculated by eddy correlation as the covariance

$$F_C = \overline{w'c'} \quad (3)$$

where  $w$  is the vertical wind velocity, the overbar indicates a time average, and the primes indicate deviations from time averaged quantities (means) (Wesely and Hart, 1985). At heights within 10 m of a very large, horizontal flat surface and in ideal conditions including fully turbulent, stationary, horizontally homogeneous flow, the fluxes measured are usually within 1% of those occurring much closer to the bulk surface (Wesely and Hart, 1985). However, there are many considerations on the practical limitations of the eddy correlation technique. It is a sophisticated method requiring several precise measuring instruments (i.e., fast response anemometers to measure vertical wind speed deviations, fast response  $\text{NO}$  analyzers for  $[\text{NO}]$  fluctuations, etc.) not well suited for routine operation. Additionally, eddy correlation flux measurements at night can be difficult because the speed of instrument response necessary to detect the flux-carrying eddies increases as the stability of the air increases when the surface is cooled (Wesely et

al., 1989). Several studies (Kaplan et al., 1988; Johansson et al., 1988; Kessel et al., 1992; Wesely et al., 1989) have shown that the results of NO emission studies using each of these techniques agree to within 30%.

## **EXPERIMENTAL**

### **Sampling Site**

Flux measurements were made in three general crop (non-irrigated) fields at the Central Crops Field Laboratory (~ 105 m MSL) which is owned by the North Carolina Agricultural Research Service and operated by North Carolina State University. The Field Laboratory is located approximately 10 km east-southeast of Raleigh, in the Upper Coastal Plain region of NC (Figure 4). The dominant soil type in each of the fields sampled is Norfolk sandy loam (Fine-Loamy, Siliceous, Thermic Typic Paleudult; Daniels et al., 1984). Each field sampled contained a different row crop (soybean, cotton, or corn) grown using fertilizer rates and management techniques representative of those commonly used by farmers throughout the Coastal Plain region of the southeastern United States.

### **Soil Analysis**

Bulk soil chemical properties from each of the three fields were obtained from composite soil samples submitted to the State Soils Laboratory of the NC Department of Agriculture (Table 1). These included humic matter content based on a 0.2 M NaOH extraction, extractable base cations using a solution composed of 0.2 M  $\text{CH}_3\text{COOH}$ ,

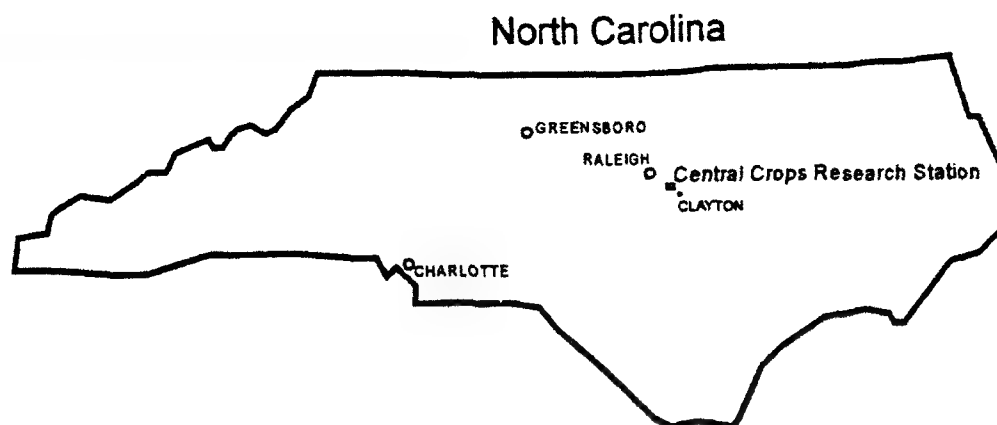


Figure 4. Map showing sampling site location near Clayton, North Carolina.

0.25 M  $\text{NH}_4\text{NO}_3$ , 0.015 M  $\text{NH}_4\text{F}$ , 0.013 M  $\text{HNO}_3$ , and 0.001 M EDTA, and exchangeable acidity using a buffer solution. Effective cation exchange capacity (ECEC; expressed on a volume basis) was obtained by summing extractable cations and exchangeable acidity. Base saturation of the ECEC was determined by  $(\text{ECEC} - \text{exchangeable acidity}) / \text{ECEC}$ .

Soil bulk density for the 0 to 15 cm depth ( $n=10$ ) was determined using the core method ( $345 \text{ cm}^3$ ) near each chamber sampling point in each field (Blake and Harge, 1986). Total soil water content and extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (2 M KCL; expressed on a weight basis) were determined on composite soil samples collected using a bucket auger (0-20 cm depth) at the end of each measurement period. Total soil water content was calculated as  $(\text{initial weight} - \text{oven dry (105 } ^\circ\text{C) weight}) / \text{oven dry weight}$ . Nitrate and  $\text{NH}_4^+$  in the 2 M KCL extract (Keeney and Nelson, 1982) was determined using standard autoanalyzer techniques (Lachat Instruments, 1990). Total soil water content at 15 bar and 0.1 bar was determined from soil moisture release curves using a pressure plate (Klute, 1986) and used as estimates of "permanent wilting point" and "field capacity", respectively (Cassel and Nielsen, 1986). The average values listed in Table 1 are based on numerous soil samples collected over the past ten years at the Central Crops

Parameter	Unit	Row Crop		
		Soybean	Cotton	Corn
pH		5.7	6.2	6.0
ECEC (a)	meq/100 cm <sup>3</sup>	2.5	3.2	2.7
Base Saturation (b)	% (by volume)	84	87	85
Acidity	meq/100 cm <sup>3</sup>	0.4	0.4	0.4
Humic Matter (c)	% (by volume)	0.5	0.5	0.6
Bulk Density	g/cm <sup>3</sup>	1.73 (±0.08)	1.67 (±0.14)	n.d.
Water Content (d)				
permanent wilting point	% (by volume)	2.8	2.8	2.8
field capacity	% (by weight)	10.8	10.8	10.8
N Application (1993 growing season)	kg/ha	21	84	173
(a) - sum of extractable base cations				
(b) - sum of extractable base cations as % of ECEC				
(c) - 0.2 M NaOH extractable humic matter				
(d) - D.K. Kassel, Dept. of Soil Science, NC State University, personal communication				

Table 1. Physical and chemical soil parameters determined for each research plot. Soil type: Norfolk sandy loam (Fine-loamy, Siliceous, Thermic Typic Paleudult).



Field Laboratory (D. K. Cassel, Department of Soil Science, North Carolina State University, personal communication). The amount of N fertilizer applied during the 1993 growing season is based on records maintained by the supervisor of the Central Crops Field Laboratory.

### **Planting and N Fertilizer Management**

Prior to planting in the Spring of 1993, each field received 21 kg N/ha as ammonium nitrate fertilizer. This broadcast application was then disked in, prior to preparation of planting beds. Actual planting followed preparation of the seed bed using a ripper-bedder to allow root penetration below a tillage pan that occurs at the 20 to 30 cm depth. Seeds were planted in the center of each bed, with approximately 1 meter spacing between beds. Cotton and corn received two side dressings of N fertilizer during the first portion of the growing season. The side dressing consisted of placing two bands of fertilizer on either side of the crop on top of the beds. No additional N fertilizer was added to the soybeans for the remainder of the growing season. The total applied ammonium nitrate fertilizer by crop was soybean, 21 kg N/ha; cotton, 84 kg N/ha; and corn, 173 kg N/ha.

### **Flux Measurements**

Nitrogen oxide fluxes were measured using a dynamic chamber technique from five randomly-selected plots (15 m x 15 m), within each crop from August 18 to September 1, 1993. Measurements were taken in the center of the interrow spaces in the soybean crop without destruction of the surrounding canopy. Measurements in the cotton and corn were taken on the center of the beds after removal of plants by cutting

the stalks at the soil surface, with minimal disturbance of the surrounding canopy. Soil temperature was monitored with a digital meter attached to a probe buried (5 cm depth) adjacent to the chamber. Air temperature was monitored with a temperature probe placed at chamber-top height, shielded from direct solar radiation. Hourly ambient  $O_3$  measurements were taken at the WRAL television transmission tower located approximately 2 km west of the Central Crops Field Laboratory.

### **Chamber Design and Operation**

The dynamic chamber used in this study is an FEP Teflon-lined cylinder (diameter  $\approx 27$  cm, height  $\approx 42$  cm, and volume  $\approx 25$  L) held in place by a stainless steel ring driven into the ground to a depth of  $\approx 5$  cm (Figure 5). The chamber was placed in the ground at least 10 hours before measurements were made. Ambient air is pumped through the chamber at a constant flow rate ( $Q = 9 \text{ l min}^{-1}$ ), and the air in the chamber is well mixed by a motor driven Teflon impeller ( $\approx 20$  cm diameter, 100 rpm). Air samples were collected after reaching steady state conditions ( $\approx 30$  minutes of operation) at the inlet and outlet ports of the chamber using Teflon bags ( $\approx 10$  L). The collection period was typically  $\approx 5$  minutes. The air samples in these bags were then immediately analyzed for their NO and  $NO_2$  concentrations.

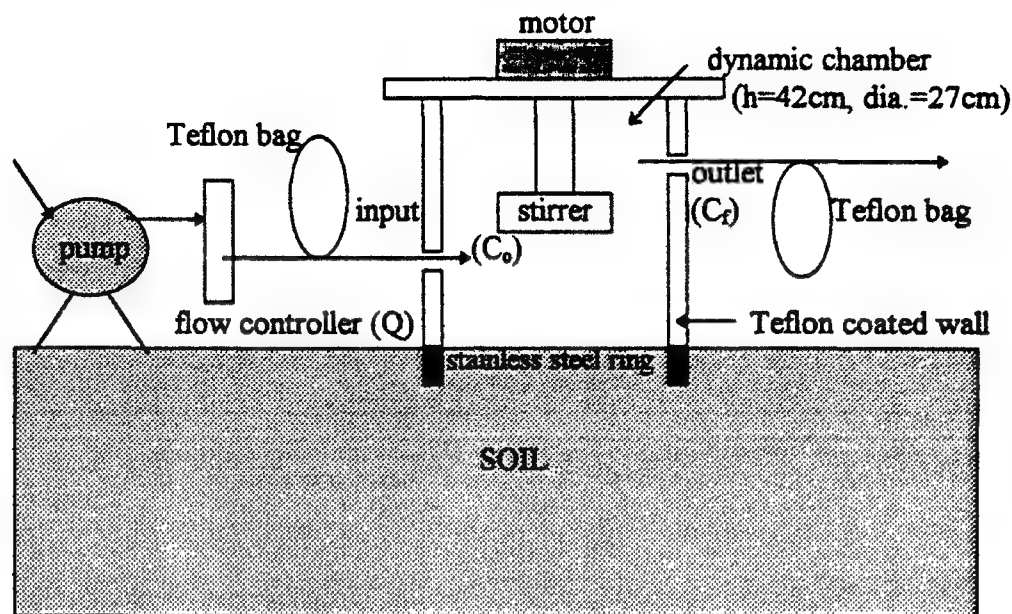


Figure 5. A schematic of the dynamic flow-through chamber. The walls and all internal surfaces are fluorinated ethylene propylene (FEP) Teflon.

### Instrumentation

Analysis of the NO concentrations in the air samples was carried out using a TECO 42S (Thermo Environmental Instruments Inc.) chemiluminescent high sensitivity NO analyzer. This instrument utilizes the reaction between NO and reagent O<sub>3</sub> which produces a chemiluminescence which is detected by a photomultiplier tube (PMT). The analyzer has an internal, gold-coated, heated (~ 325 °C) molybdenum converter. Analysis of the NO<sub>2</sub> concentrations in the ambient air samples was carried out using a LMA-3 Luminol-based NO<sub>2</sub> analyzer (Scintrex Ltd.). The LMA-3 analyzer operates by detecting the chemiluminescence produced when NO<sub>2</sub> encounters a surface wetted with a

specially formulated proprietary solution (Luminol). The monitor does not require prior conversion of  $\text{NO}_2$  to  $\text{NO}$  as do other chemiluminescence detectors. The Luminol solution is oxidized producing chemiluminescence ( $< 425 \text{ nm}$ ) and a PMT detects the intensity of the light. The signal from the PMT is directly proportional to the concentration of  $\text{NO}_2$ . The instruments were periodically calibrated according to protocol using a mixture of 0.105 ppm  $\text{NO}$  in  $\text{N}_2$  and a mixture of 0.116 ppm of  $\text{NO}_2$  in  $\text{N}_2$  (Scott Specialty Gases, Inc., Plumsteadville, PA). Detection limits for these instruments under laboratory conditions are cited at 50 parts per trillion volume (pptv) for  $\text{NO}$  (Thermo Environmental Instrument, Inc. Model 42S, 1992) and  $\approx 5$  pptv for  $\text{NO}_2$  (LMA-3 Operators Manual, 1987). Additional detail concerning the instrumentation are described elsewhere (Kim et al., 1993; Dickerson et al., 1984; Scintrex Ltd., 1989).

### Flux Calculation

The mass balance for  $\text{NO}$  in the chamber (Kaplan et al., 1988) is given by

$$\frac{dC}{dt} = \left( \frac{Q [C]_0}{V} + \frac{J A}{V} \right) - \left( \frac{L A [C]_f}{V} + \frac{Q [C]_f}{V} \right) + R \quad (4)$$

where

$A$  = soil surface area covered by the chamber;

$V$  = volume of the chamber;

$Q$  = flow rate through the chamber;

$J$  = emission flux;

$C$  =  $\text{NO}$  concentration in the chamber;

$[C]_0$  =  $\text{NO}$  concentration at the inlet of chamber;

$[C]_f$  = NO concentration at the outlet of chamber,

$L$  = loss term by chamber wall per unit area assumed first order in  $[C]$ ;

$R$  = chemical production/destruction rate in the chamber.

For a well-mixed chamber  $[C]_f$  may be assumed to be equal to the NO concentration in the chamber.

NO is oxidized rapidly in the ambient atmosphere. This rapid oxidization requires that the calculated NO fluxes be corrected for possible chemical reactions within the chamber. Generally, three oxidants have a major role in the oxidation of atmospheric NO. They are  $O_3$ ,  $HO_2$  and  $RO_2$  (Finlayson-Pitts and Pitts, 1986).  $NO_2$  flux (even negative flux) is typically much lower than NO flux from soils (Slemr and Seiler, 1991; Johansson and Granat, 1984) and the low ambient concentrations of  $NO_2$  at the measurement site are not expected to produce significant quantities of NO in the chamber. Thus,  $R$  in equation (4) can be written as:

$$R = - (k_1[O_3] + k_2[HO_2] + k_3[RO_2]) [NO] = - \left( \sum_{i=1}^3 k_i R_i \right) C \quad (5)$$

where  $R_i$  is each reactant species and  $k_1$  ( $= 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ),  $k_2$  ( $= 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) and  $k_3$  ( $= 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) are reaction rates for  $O_3$ ,  $HO_2$  and  $RO_2$  with NO, respectively. Equation (4) becomes:

$$\frac{dC}{dt} = - \left( \frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^3 k_i R_i \right) C + \left( \frac{J}{h} + \frac{Q[C]_0}{V} \right) \quad (6)$$

where  $h$  ( $\approx 42 \text{ cm}$ ) is the height of the chamber. Solving equation (6) for the NO flux,  $J$ , under steady state condition yields:

$$J = h \left\{ \frac{Q}{V}(C_f - C_o) + \left( \frac{L}{h} + \sum_{i=1}^3 k_i R_i \right) C_f \right\} \quad (7)$$

Surface O<sub>3</sub>, RO<sub>2</sub> and HO<sub>2</sub> concentrations are necessary for the calculation of the chemical loss term. RO<sub>2</sub> concentrations have been calculated at Scotia, PA (Trainer et al., 1991), and site SONIA (Hartsell, 1993); and measured at site ROSE, AL (Cantrell et al., 1992). All are similar in magnitude. Maximum RO<sub>2</sub> concentrations for the three rural sites during the high-pressure period in summer were on the order of 10<sup>9</sup> molecules cm<sup>-3</sup>. For site SONIA, the average noon time RO<sub>2</sub> concentration was calculated to be about 30 pptv (7.4 x 10<sup>8</sup> molecule cm<sup>-3</sup>). HO<sub>2</sub> concentrations are expected to be ~30 % of RO<sub>2</sub> and average daytime O<sub>3</sub> concentrations at the WRAL Tower were about 37 ppbv (Trainer et al., 1991; Trainer et al., 1987). However, O<sub>3</sub>, RO<sub>2</sub> and HO<sub>2</sub> are rapidly deposited on the interior surface of the chamber, and the enclosed vegetation and exposed soil. Near surface O<sub>3</sub> concentrations used for the flux calculation were assumed to be equal to the nighttime O<sub>3</sub> average (≈ 5 ppbv) measured at the WRAL tower. Estimates of the near-surface concentrations of RO<sub>2</sub> and HO<sub>2</sub> (approximately 60 % of ambient levels) were based on model projections (Trainer et al., 1987; Hartsell, 1993).

The loss of NO by reaction with the Teflon coated-wall of the chamber was estimated by taking the difference between the combined surface loss as proposed by Kaplan et al. (1988) and the chemical loss in the chamber as calculated by equation (2). This approach calculated a wall loss, L, of 0.02 cm s<sup>-1</sup>. The wall loss for NO<sub>2</sub> was estimated as 0.08 cm s<sup>-1</sup>.

## RESULTS

### Site Characteristics

$\text{NO}_x$  flux measurements were made in an agriculturally-managed soil with three different crops reflecting three different levels of applied nitrogen (soybean, 21 kg/ha; cotton, 84 kg/ha; and corn, 173 kg/ha). A data summary is given in Table 2. For the soybean field, the soil water content ranged from 1.80% to 7.80% with an average of  $3.49 \pm 2.44\%$ . The cotton field soil water content ranged from 1.78% to 3.29%, for an average of  $2.63 \pm 0.74\%$ . Corn field moisture values were 0.58% to 1.75% with an average of  $1.10 \pm 0.60\%$ . There was essentially no rainfall during the measurement period and the three fields were not irrigated. The soybean and cotton crops survived because their roots were able to access available water in the subsoil. The corn crop, however, had already failed prior to the start of our measurements. Soil temperatures ranged from 23.3 to 32.5 °C, with an average of  $25.6 \pm 1.4$  °C for the soybean field, and  $27.5 \pm 7.5$  °C for the cotton field.

### NO Flux

Figure 6 shows the composite hourly NO flux. Overall average NO flux rates increased proportionally to the level of applied fertilizer nitrogen in each of the fields. For the corn field, KCl extractable  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ranged from 3 to 19 mg N kg<sup>-1</sup>. The soybean field measurements revealed an NO flux of 1.79 (range -1.0 to 6.9) ng N m<sup>-2</sup> s<sup>-1</sup>, the cotton field average NO flux was 3.77 (range -0.1 to 38.0) ng N m<sup>-2</sup> s<sup>-1</sup>, and the corn field average NO flux was 8.05 (range -0.5 to 52.8) ng N m<sup>-2</sup> s<sup>-1</sup>.

Crop Field	(a)		(b)		(c)		(d)	
	Soil Temp (C)		Air Temp (C)		Total Extractable Nitrogen		Air Carrier NO Flux NO2 Flux	
Soybean	Average	25.6		29.7	0.74	3.49	1.79	-0.54
	Std Dev	1.4		3.4	0.19	2.44	1.92	4.65
	Min	23.3		22.2	0.55	1.8	-1.01	-25.98
	Max	27.4		33.5	0.97	7.8	6.86	5.35
Cotton	Average	27.5		28.2	1.53	2.63	3.77	-4.43
	Std Dev	2.5		6.4	0.8	0.74	5.89	9.42
	Min	23.6		17.5	0.79	1.78	-0.07	-38.71
	Max	32.5		39	2.89	3.29	38.02	25.86
Corn	Average	n/a		35	9.59	1.1	8.05	6.64
	Std Dev	"		3.8	8.55	0.6	12.94	14.12
	Min	"		24	3.92	0.58	-0.54	-30.27
	Max	"		40	19.43	1.75	52.79	29.18

(a) - soil temperature measured at 5 cm depth adjacent to chamber.

(b) - air temperature measured at chamber height

(c) - Units are mg-N/kg

(d) - Units are ng N m<sup>-2</sup> s<sup>-1</sup>.

Table 2. Data summary for the 18 Aug - 1 Sep 1993 measurement period.



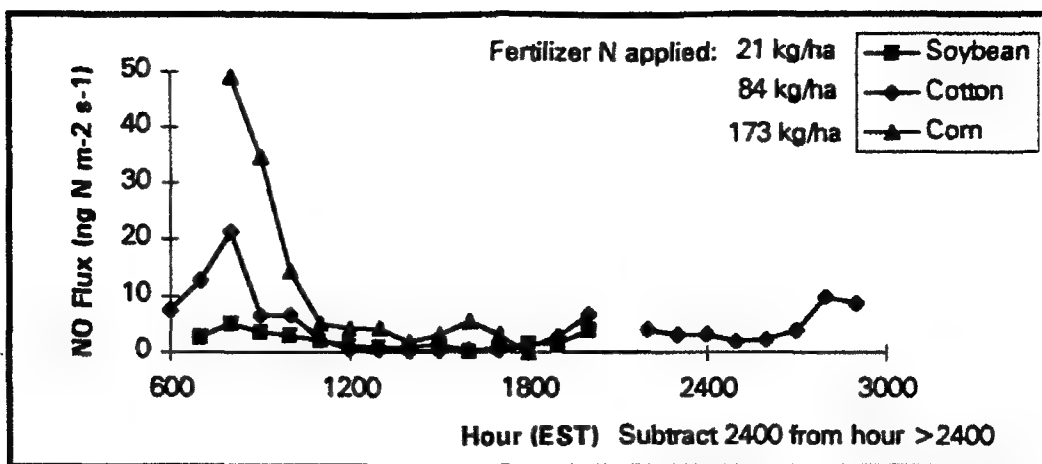


Figure 6. Composite hourly NO flux as a function of nitrogen fertilizer applied to each crop.

A plot of the composite soil temperature vs NO flux for the soybean and cotton crops is shown in Figure 7. The plotted data points were obtained by averaging over equally-spaced ranges of soil temperature. An inverse exponential relationship is exhibited by the data, with  $R^2 = 0.76$  for both soybean and cotton (no corn data).

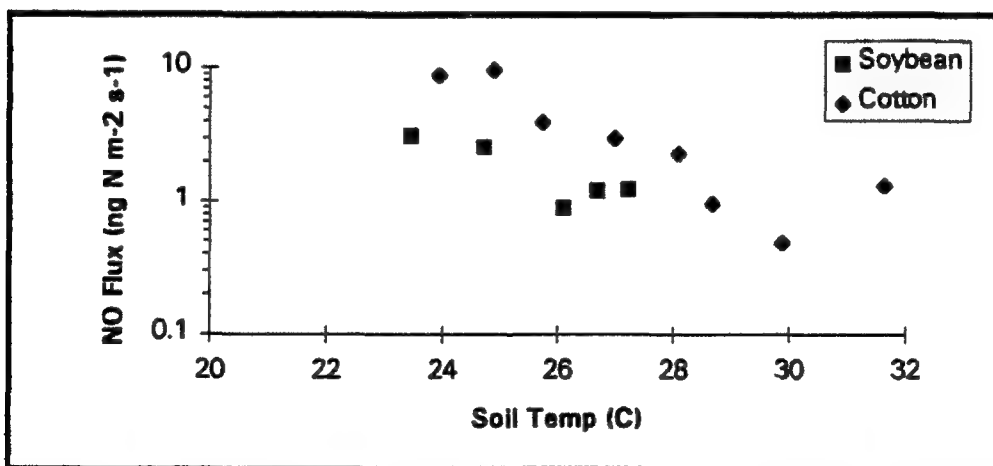


Figure 7. Composite soil temperature vs NO flux as a function of fertilizer nitrogen applied to each crop.

## NO<sub>2</sub> Flux

The composite hourly NO<sub>2</sub> flux by crop type is shown in Figure 8. The overall average fluxes were negative for the soybean and cotton crops, with the soybean NO<sub>2</sub> flux averaging  $-0.54 \text{ ng N m}^{-2} \text{ s}^{-1}$ ; the cotton flux mean was  $-4.43 \text{ ng N m}^{-2} \text{ s}^{-1}$ . The overall average NO<sub>2</sub> flux in the corn location was  $6.64 \text{ ng N m}^{-2} \text{ s}^{-1}$ . Deposition and possible loss in the chamber is indicated by the 0800 EST minima in the NO<sub>2</sub> data from all three crops. By midday, NO<sub>2</sub> flux approaches zero in both the soybean and cotton locations, but approached an average of  $\sim 10 \text{ ng N m}^{-2} \text{ s}^{-1}$  in the corn location. We currently have no explanation for this corn NO<sub>2</sub> flux signature.

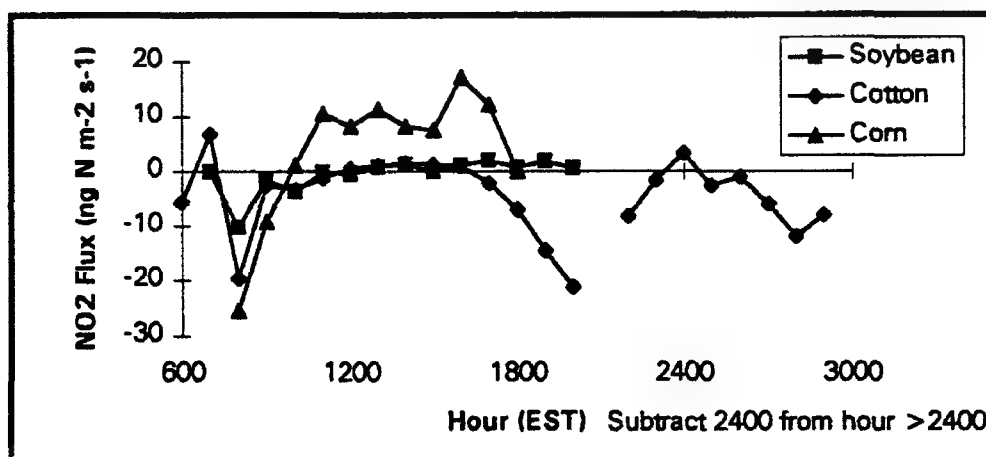


Figure 8. Composite hourly NO<sub>2</sub> flux as a function of fertilizer nitrogen applied to each crop.

## DISCUSSION

The accuracy of the NO<sub>x</sub> fluxes calculated here rests on the assumption that the ozone concentration in the ambient air used as the carrier gas in the chamber is

adequately represented by the near surface nighttime average measured at another rural site in North Carolina (Kim et al., 1994). Additionally, the presence of the chamber itself, while shielded by the crop canopy in most cases, could result in elevated temperatures inside the chamber. This in turn could influence soil NO flux. However, since the flux equation used accounts for loss due to reactions within the chamber, as well as wall losses, and assumes steady state conditions exist in the chamber at the time of measurement, the resulting calculated flux values are conservative in nature and biased low (underestimated) if any of the above assumptions are incorrect.

The composite hourly NO flux signature evident in these results mirror observations of other field measurements (Shepherd et al., 1991; Valente and Thornton, 1993; Kim et al., 1994), with the morning peak, and later leveling-off to a relatively constant value. The morning peak in NO flux for this data occurred earlier in the day than normal, most likely evidence of the extreme moisture stress present on the soil microbes (Anderson and Levine, 1987). The mechanism responsible for the existence of the peak itself is still unclear. One possible explanation is that the roots of the plants exude organic substances during the morning hours just after sunrise. These compounds are then utilized by denitrifying bacteria which reduce  $\text{NO}_3^-$  and, subsequently, NO will be produced more rapidly than predicted by the soil temperature (Johansson and Granat, 1984). As this exudate is consumed, the NO flux decreases.

The negative exponential relationship observed between soil temperature and NO flux (Figure 7) suggests the presence of extreme moisture stress on the soil microbes responsible for NO production (Anderson and Levine, 1987). Williams et al. (1987) reported significantly reduced NO emissions when the soil moisture level is reduced below about 10%. Moisture values ranged from 0.58 to 3.49 % during these experiments.

NO is rapidly oxidized to NO<sub>2</sub> by reaction with O<sub>3</sub> in the atmosphere, especially during the night. Therefore, significant concentrations of NO and O<sub>3</sub> are usually not found in the same air mass. Additionally, O<sub>3</sub> does not accumulate during a photochemical air pollution episode until the NO concentration has fallen to low values (Findlayson-Pitts and Pitts 1986). A negative correlation was observed between NO flux and ambient O<sub>3</sub> concentrations in all three crop fields ( $R^2=0.34$  for soybeans, 0.31 for cotton and 0.71 for corn, Figure 9). O<sub>3</sub> regulates the ambient NO concentration and ambient NO concentration is related to NO flux through the NO compensation point (Slemr and Seiler, 1991; Kim et al. 1994). For this reason, NO flux from soil may also be negatively correlated with ambient O<sub>3</sub> concentration. Moreover, these results suggest that NO emission from the soils increases ambient NO concentrations (Figure 10).

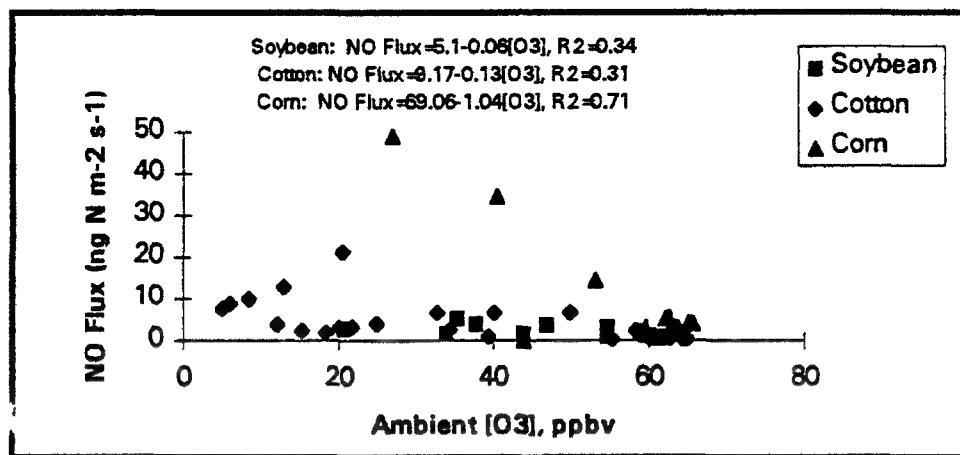


Figure 9. Composite ambient ozone concentration vs NO flux as a function of fertilizer nitrogen applied to each crop.

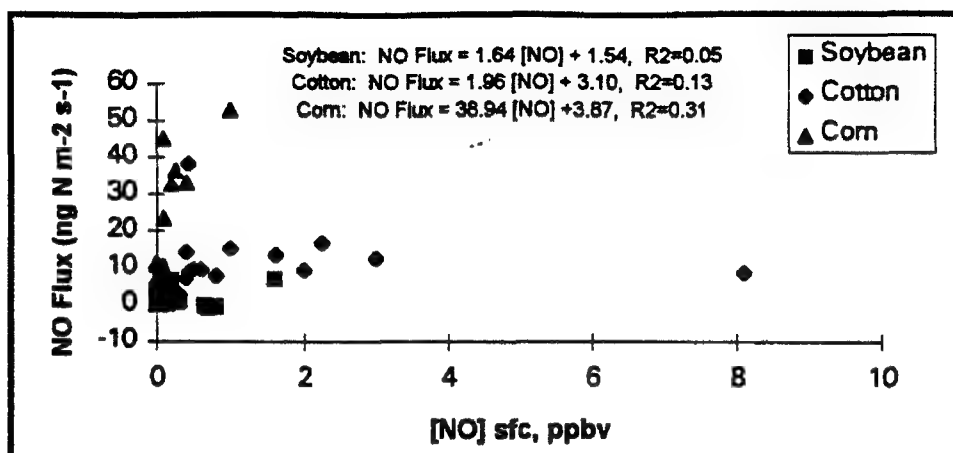


Figure 10. Composite surface NO concentration vs NO flux as a function of fertilizer nitrogen applied to each crop.

These preliminary results suggest that the flux of NO from agricultural soil appears to be substantially larger than those from a North Carolina non-agricultural soil (average 1.79 ng N m<sup>-2</sup> s<sup>-1</sup>, Kim et al., 1994) during summer. NO flux increased with increased application of N fertilizer. Further research needs to be done concerning on-going reactions possibly existing in the chamber, preferably in lower ozone conditions with adequate soil moisture. Nevertheless, these preliminary data seem to call into question current methodologies for managed agricultural practices for their role in subsequent ambient air quality.

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## SECTION II. NITROGEN OXIDE FLUXES FROM AGRICULTURAL SOILS DURING WINTER FALLOW IN THE UPPER COASTAL PLAIN OF NORTH CAROLINA

### Abstract

The fluxes of NO and NO<sub>2</sub> from a fallow field to the atmosphere were measured. Two identical chambers were used, with ambient air as the carrier gas in one, and nitrogen as the carrier gas in the other. In laboratory experiments, the use of nitrogen carrier gas significantly increased NO fluxes from soil samples; nitrogen carrier gas was used in these field measurements to assess the possible NO flux potential (a theoretical upper limit of NO flux possible) of the soil. Overall average NO flux rates increased proportionally to carbon/nitrogen ratio of the plant residue plowed back into the soil at the end of the previous growing season. The soybean, cotton and corn field measurements revealed an average NO flux of 10.23 (range -10.77 to 133.06) ng-N m<sup>-2</sup> s<sup>-1</sup>; 5.07 (range -11.71 to 109.55) ng-N m<sup>-2</sup> s<sup>-1</sup>; and 3.68 (range -17.51 to 40.39) ng-N m<sup>-2</sup> s<sup>-1</sup> respectively, using the ambient air carrier gas. The winter measurements suggest that significant fluxes are generated during fallow periods when the plant residue is mixed back into the soil, a common agricultural practice.

## INTRODUCTION

The major source of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) in the atmosphere is fossil fuel combustion (Logan, 1983). However, recent studies indicate that biogenic emissions of  $\text{NO}_x$  (predominately  $\text{NO}$ ) may also represent a significant source (Williams and Fehsenfeld, 1991). Measurements of soil flux of  $\text{NO}_x$  show that in some cases, comparable emission rates exist between anthropogenic emissions in urban areas and agricultural areas (Williams et al., 1988; Williams et al., 1992). Understanding and quantifying soil emissions of  $\text{NO}_x$  is of importance in understanding the formation of tropospheric ozone. This is particularly true in rural areas where man-made sources of  $\text{NO}_x$  are often minimal and ozone production may be dependent upon biogenic sources of  $\text{NO}_x$  (Valente and Thornton, 1993).

General circulation models have been used to predict the distributions of tropospheric  $\text{NO}_x$  and ozone (Penner et al., 1991), but correctness of the source areas is uncertain due to large spatial and temporal variation in soil  $\text{NO}_x$  efflux (Davidson et al., 1991). Attempts to correlate soil  $\text{NO}_x$  emissions with soil parameters in order to improve the predictability of soil  $\text{NO}_x$  efflux have produced mixed results. Some studies (Johansson and Granat, 1984; Williams et al., 1987, 1988) show strong correlation between  $\text{NO}_x$  emissions and soil temperature. However, similar correlation analysis of soil temperature, soil chemistry, and soil  $\text{NO}_x$  emissions by other researchers have not indicated a relationship (Anderson and Levine, 1987; Slemr and Seiler, 1991; Johansson et al., 1988).

Relatively few measurements of emissions of soil  $\text{NO}_x$  have been made in the southeast United States, except for Williams and Fehsenfeld (1991) and Valente and Thornton (1993) in Tennessee, Kim et al. (1994) and Aneja et al., (1994) in North

Carolina. A further understanding of the importance of biogenic  $\text{NO}_x$  emissions in the formation of ozone in this region is needed since approximately 40% of the ozone non-attainment areas in the United States are found in the Southeast (Lindsay et al., 1989) and rural summertime ozone concentrations are among the highest recorded in the US (Pinkerton and Lefohn, 1988). Additionally, Valente and Thornton (1993) suggested that soils may be emitting about 60% as much  $\text{NO}_x$  as from all the utilities in the state of Tennessee during the summer months. The National Acid Precipitation Assessment Program (NAPAP) 1985 (Placet et al., 1990) has estimated that 11% of total  $\text{NO}_x$  emissions comes from natural sources. However, Valente and Thornton (1993) found soil  $\text{NO}_x$  emissions equalling 19.1% of the summertime total  $\text{NO}_x$  emissions estimate.

In this paper we present preliminary soil  $\text{NO}_x$  measurements made in late Winter/early Spring 1994, herein referred to as winter, in the Upper Coastal Plain of North Carolina, and also some preliminary observations concerning process-based mechanisms controlling  $\text{NO}_x$  emission. The objectives are to assess the impact of crop residue and past fertilizer application rates on soil  $\text{NO}_x$  emissions. During the winter season, ambient ozone is comparatively low, moisture is more abundant, and soil temperatures are moderate. These conditions provide a good opportunity to test the continuously-stirred tank reactor (CSTR) chamber method under low ozone conditions. To assess the  $\text{NO}_x$  flux potential of the soil, we simultaneously made  $\text{NO}_x$  flux measurements in a co-located chamber using nitrogen as the carrier gas. This data will be incorporated in an inventory of biogenic  $\text{NO}_x$  to be used in modeling ozone distribution throughout the Coastal Plains physiographic region of the Southeastern United States.

## MEASUREMENT TECHNIQUE

### Chamber Design and Operation

The soil  $\text{NO}_x$  measurements were performed using the dynamic chamber technique outlined in section II. For the winter measurements, two identical chambers were placed within  $\approx 20$  cm of each other. The first chamber utilized ambient air as the carrier gas. Prepurified nitrogen was utilized as the carrier gas in the second chamber, with all other conditions and sampling techniques remaining constant. Hourly samples were taken in FEP Teflon bags from each chamber simultaneously. Published results from laboratory studies (Lipschultz et al., 1981; Johansson and Granat, 1984) have shown that NO flux from soil in the presence of a nitrogen atmosphere can increase by several orders of magnitude. We decided to use this observation in an attempt to measure the NO flux potential of each field. We define NO potential as the upper limit of NO flux possible from a field for the given soil water content, soil temperature, and available nitrogen that exist at the time of sampling. Use of nitrogen as the carrier gas offers the additional advantage of eliminating any secondary reactions within the chamber.

### Instrumentation

Analysis of the NO and  $\text{NO}_2$  concentrations in the air and nitrogen samples was carried out using a TECO 42S chemiluminescent high sensitivity NO analyzer (Thermo Environmental Instruments Inc.), and a LMA-3 Luminol based  $\text{NO}_2$  analyzer (Scintrex Ltd.) as discussed in section II. These samples were analyzed within 3 minutes of each other.

## Flux Calculation

Fluxes of NO and NO<sub>2</sub> were calculated using a mass balance equation that also accounted for reactions within the chamber (in the ambient air carrier). Details and theory behind this flux equation are discussed in Section II.

## Sampling Site

Flux measurements in the winter experiments were made in the same three general crop (non-irrigated) fields at the Central Crops Research Station (105 m MSL) described in Section II. Prior to planting in the Spring of 1993, each field received 21 kg N/ha as ammonium nitrate fertilizer. This broadcast application was then disked in, prior to preparation of planting beds. Actual planting followed preparation of the seed bed using a ripper-bedder to allow root penetration below a tillage pan that occurs at the 20 to 30 cm depth. Seeds were planted in the center of each bed, with approximately 1 meter spacing between beds. Cotton and corn received two side dressings of N fertilizer during the first portion of the growing season. The side dressing consisted of placing two bands of fertilizer on either side of the crop on top of the beds. No additional N fertilizer was added to the soybeans for the remainder of the growing season.

Following harvesting in the Fall of 1993, the crop stubble was leveled using a mower and the residue disked into the surface soil. Winter wheat was planted as the cover crop, and was approximately 5 cm in height during the sampling period.



## Soil Analysis

Total soil water content and extractable ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) (2 M KCl; expressed on a weight basis) were determined on composite soil samples collected from the center of the chamber placement footprint using a bucket auger (0-20 cm depth) at the end of each measurement period. Total soil water content was calculated as (initial weight - oven dry (105 °C) weight) / oven dry weight. Nitrate and ammonium in the 2 M KCL extract (Keeney and Nelson, 1982) was determined using standard autoanalyzer techniques (Lachat Instruments, 1990). Soil temperature was measured using a thermocouple probe inserted approximately 5 cm into the soil adjacent to the chamber. Air temperature was measured by inserting a probe into the chamber outlet immediately after removing the sample bag.

## Flux Measurements

The three sampled crop fields were divided into 15 randomly-selected plots, approximately 15 m by 15 m. Samples were taken from five of these plots. The chambers were placed in the center of the plot enclosing the cover crop. Simultaneous measurements of NO and NO<sub>2</sub> were taken from February 7 to March 23, 1994, normally from 0600 until 2000 EST. One 24 hour experiment in each crop location was conducted to discern the diurnal profile of NO<sub>x</sub> flux.

## RESULTS

Soil water contents were much higher during the winter measurements than during the summer experiment (Section I, Table 2), with the percent water-filled pore space (%WFPS) in the optimum range for NO production (Davidson, 1991). The %WFPS averages were  $47.2 \pm 3.2$  in the soybean field,  $54.9 \pm 6.1$  in the cotton field, and  $34.1 \pm 7.2$  in the corn field. Total extractable nitrogen was relatively constant, averaging  $4.13 \pm 0.92$  mg-N/kg in the soybean location,  $6.49 \pm 3.42$  mg-N/kg in the cotton location, and  $4.54 \pm 0.41$  mg-N/kg in the corn location.

### NO Flux

Ambient air as the carrier gas. Figure 1 shows the composite hourly NO flux by previous crop for the winter measurement period.

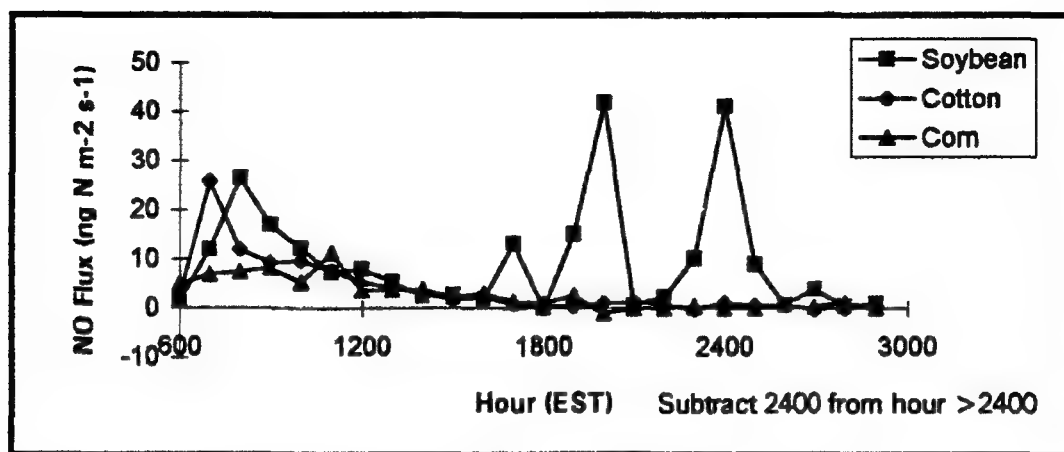


Figure 1. Composite hourly NO flux as a function of prior crop residue incorporated into the soil after harvest in 1993, using ambient air as the carrier gas.

The features evident in the summer measurements (Section I, Figure 6) are duplicated in this chart: an early morning peak in NO flux, followed by a decrease to near zero flux in the late afternoon and early evening hours. The largest peak in NO flux is associated with the soybean and cotton residue, but no peak is observed for the corn residue. The peaks in NO flux during the evening hours for the soybean residue was observed during the diurnal profile measurement, and represent only one data point. However, we don't believe these values are anomalies, since the adjacent points reflect the trend. We currently have no explanation for their peaks' existence. NO flux averaged  $10.2 \pm 20.1$  (range -10.8 to 133.1)  $\text{ng N m}^{-2} \text{s}^{-1}$  in the soybean location,  $5.1 \pm 12.6$  (range -11.7 to 109.6)  $\text{ng N m}^{-2} \text{s}^{-1}$  in the cotton location, and  $3.7 \pm 6.0$  (range -17.5 to 40.4)  $\text{ng N m}^{-2} \text{s}^{-1}$  in the corn location (Table 1). Fourteen of 245 (5.7%) data points suggested NO deposition.

The relationship between composite soil temperature and NO flux for the winter measurements (data points averaged over equally-spaced temperature bands) is less clear than that observed in the summer data (Section I, Figure 7). In the presence of ambient air, soil NO flux decreased exponentially with increasing soil temperature for both soybean ( $R^2=0.74$ ) and cotton ( $R^2=0.74$ ) (Figure 2), suggesting an NO emission precursor becoming limiting with increased temperature.

Crop Field	(a)		(b)	(c)	(d)	(e)		(e)		(e)	
	Soil Temp (C)	Air Temp (C)		Total Extractable Nitrogen		NO Flux	Air Carrier NO2 Flux	NO Flux	N2 Carrier NO2 Flux	NO Flux	N2 Carrier NO2 Flux
Soybean	Average	8.41	12.01	4.13	47.18	10.23	-14.13	9.18	0.88		
	Std Dev	3.55	5.56	0.92	3.19	20.15	26.28	12.03	1.58		
	Min	0.90	0.00	3.08	43.10	-10.77	-141.04	0.00	0.00		
	Max	14.20	23.90	5.25	51.50	133.06	38.45	52.23	9.56		
Cotton	Average	10.00	13.22	6.49	54.95	5.07	-5.97	6.22	0.40		
	Std Dev	5.25	9.02	3.42	6.09	12.56	11.44	8.93	0.67		
	Min	3.30	1.70	3.23	48.00	-11.71	-83.49	0.34	0.00		
	Max	21.00	31.50	10.28	62.20	109.55	15.11	42.43	3.91		
Corn	Average	12.45	16.99	4.54	34.10	3.68	-8.08	8.31	0.84		
	Std Dev	4.70	9.21	0.41	7.21	5.96	11.23	17.12	0.71		
	Min	3.30	-1.50	4.20	26.00	-17.51	-64.55	0.00	0.00		
	Max	20.70	32.20	5.16	43.40	40.39	25.33	96.90	3.44		

(a) - soil temperature measured at 5 cm depth adjacent to chamber.

(b) - air temperature measured inside the chamber

(c) - Units are mg-N/kg

(d) - Percent Water-Filled Pore Space

(e) - Units are ng N m<sup>-2</sup> s<sup>-1</sup>.

Table 1. Data summary for the 7 Feb - 18 Mar 1994 measurement period.

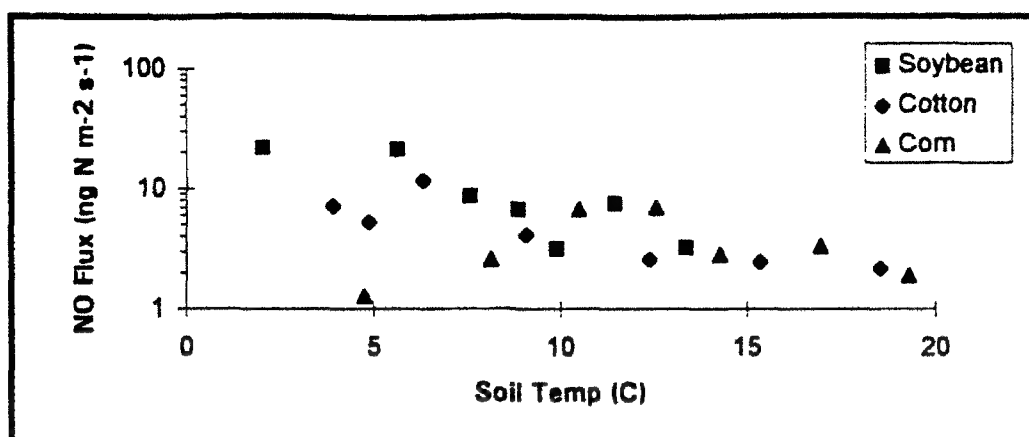


Figure 2. Composite soil temperature vs NO flux as a function of prior crop residue incorporated into the soil after harvest in 1993, using ambient air as the carrier gas.

The corn data exhibits a more complex relationship. Fitting an exponential curve to the overall corn trend returns an  $R^2$  of only 0.03. This suggests the possible presence of another process confounding the NO emission/soil temperature relationship in the corn location.

Nitrogen as the carrier gas. To test the hypothesis of the NO flux potential, we used nitrogen as the carrier gas in a second chamber adjacent to the ambient air chamber. The ambient air and nitrogen chambers were sampled simultaneously. These samples were then analyzed within three minutes of each other. The composite hourly NO flux as a function of the previous crop is shown in Figure 3.

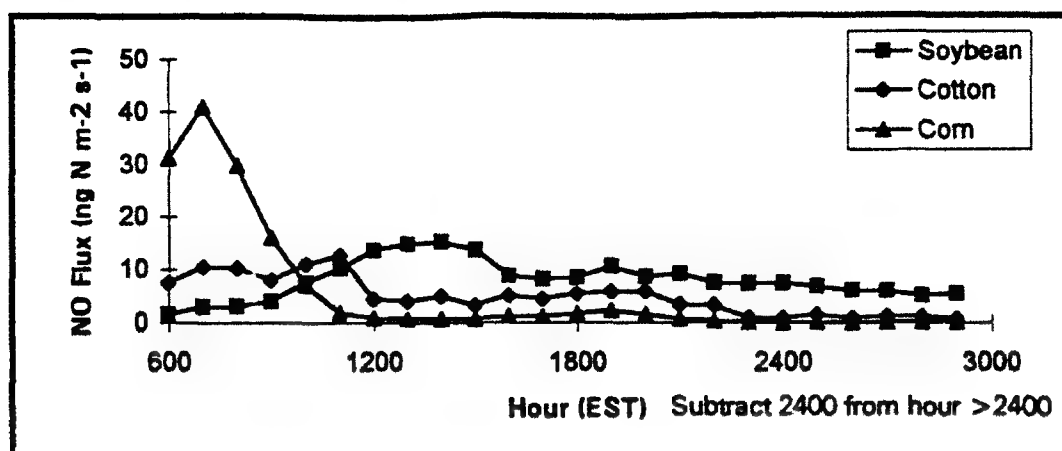


Figure 3. Composite hourly NO flux as a function of prior crop residue incorporated into the soil after harvest in 1993, using nitrogen as the carrier gas.

There is a substantial difference in the temporal signature and overall flux values when compared to Figure 1. The corn residue now reveals an early morning peak in NO flux, with a rapid decrease to near zero flux by midday. The soybean residue NO flux signature shows a steady increase until mid-afternoon, declining to a mean of approximately  $10 \text{ ng N m}^{-2} \text{ s}^{-1}$ . The cotton residue NO emissions also depart from the earlier pattern, with a morning increase, leveling to roughly  $5 \text{ ng N m}^{-2} \text{ s}^{-1}$  during the afternoon and evening hours.

An analysis of the composite soil temperature versus NO flux with nitrogen as the carrier gas (Figure 4) suggests the interaction of the C/N ratio of the crop residue with temperature. Here the soybean residue (C/N ~15:1) produced an exponentially increasing NO flux with increasing soil temperature ( $R^2=0.76$ ), suggesting that nitrogen was not limiting in this instance. As soil temperature increased, microbial activity and subsequent nitrification increased as well, producing larger NO emissions. The cotton data shows no clear trend ( $R^2=0.05$ ), possibly reflecting the comparability of the cotton C/N ratio (~32:1) to the break-even value separating nitrogen immobilization from nitrification. Fitting the exponential model to the overall corn data returns an  $R^2$  of 0.25,

with a slight negative trend. Since corn residue has a C/N ratio well into the nitrogen immobilization range (~50:1), an increase in soil temperature and subsequent microbial activity may reduce the nitrogen available for nitrification, decreasing NO emissions.

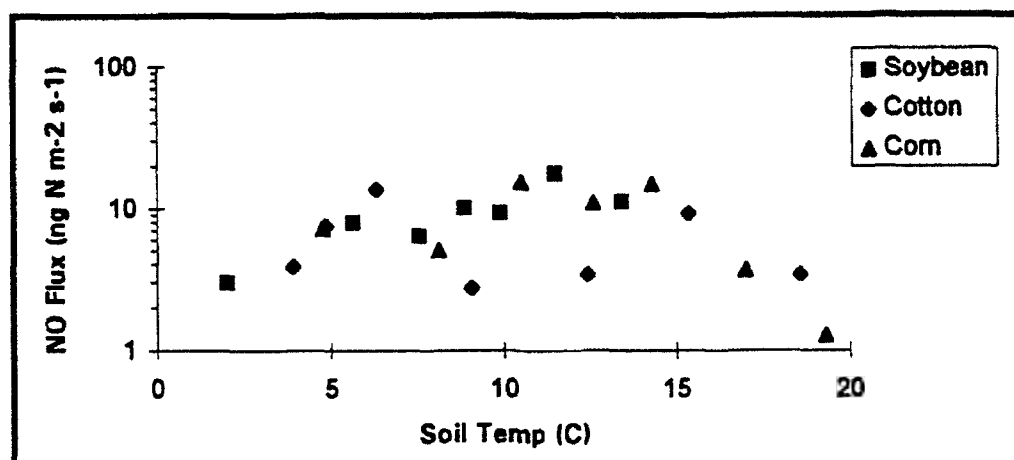


Figure 4. Composite soil temperature vs NO flux as a function of prior crop residue incorporated into the soil after harvest in 1993, using nitrogen as the carrier gas.

### NO<sub>2</sub> Flux

Figure 5 shows the composite hourly NO<sub>2</sub> flux by crop for the ambient air measurements. Except for the peak values in the soybean diurnal experiment, deposition was normally observed in the ambient air carrier data ( $202/245 = 82.4\%$ ).

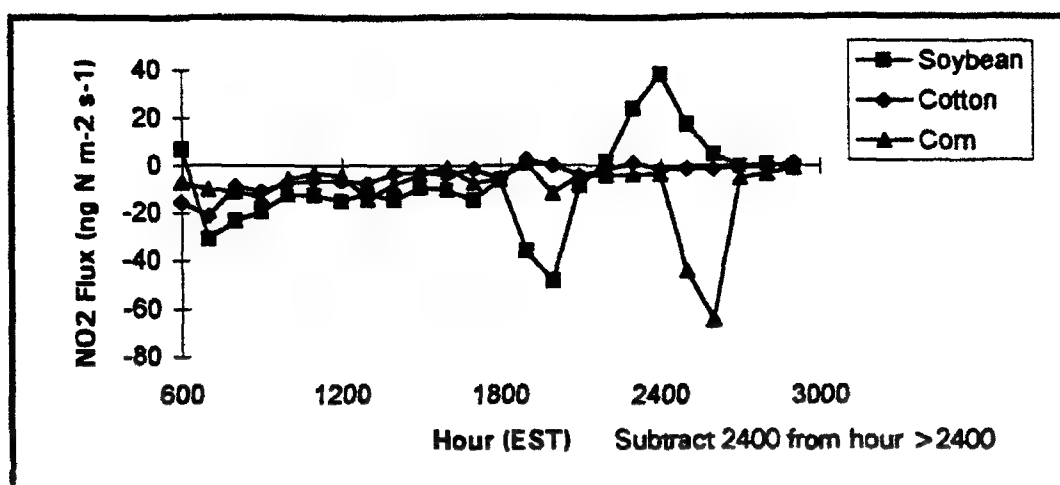


Figure 5. Composite hourly  $\text{NO}_2$  flux as a function of prior crop residue incorporated into the soil after harvest in 1993, using ambient air as the carrier gas.

Figure 6 shows the composite hourly  $\text{NO}_2$  flux by crop for the nitrogen carrier experiments. While much smaller than the  $\text{NO}$  flux,  $\text{NO}_2$  emission is evident in this case (averaging less than  $1 \text{ ng N m}^{-2} \text{ s}^{-1}$ ), with the late night peak of  $\text{NO}_2$  emission over the soybean field revealed here in the nitrogen carrier experiments also evident in the adjacent ambient air carrier measurements. In this preliminary analysis, we have not yet investigated the mechanism(s) responsible for this late-night peak. This  $\text{NO}_2$  emission signature is in contrast to other findings in the literature, where  $\text{NO}_2$  deposition is usually reported.



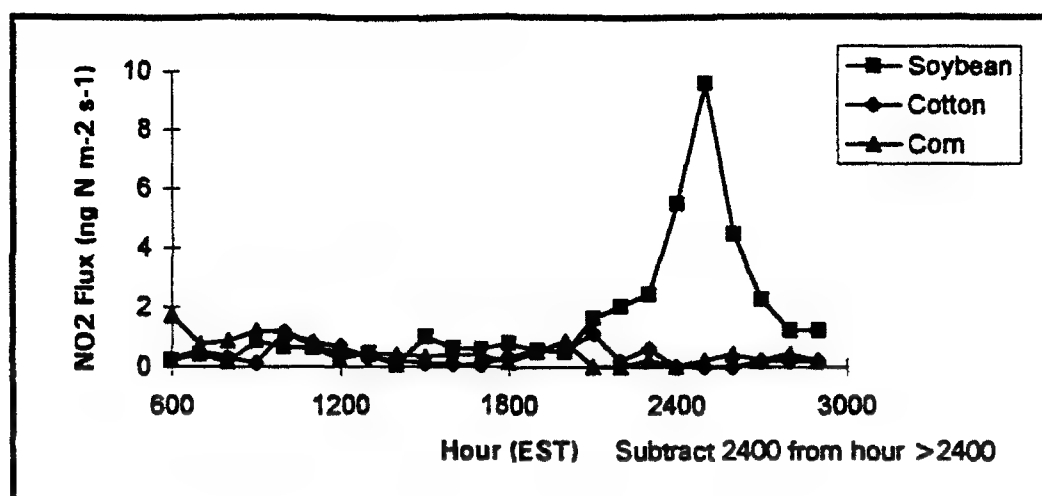


Figure 6. Composite hourly NO<sub>2</sub> flux as a function of prior crop residue incorporated into the soil after harvest in 1993, using nitrogen as the carrier gas.

## DISCUSSION

February and March are not considered to be high ozone months in North Carolina; so ozone, in the ambient air carrier experiments, should have been less a confounding factor. The calculated fluxes should therefore be representative of the NO flux from the surface of the field. The similar NO flux signatures apparent in both the summer and winter ambient air measurements give confidence in both our measurement technique and flux determinations.

The ambient air carrier composite NO flux temporal signatures suggest the effect of available nitrogen and soil temperature on microbial biomass, with the soybean flux values often exceeding those of both cotton and corn. The nitrogen carrier NO flux signatures provide stronger evidence for this hypothesis.

During this fallow agricultural-management phase, all the original nitrogen from the previous fertilizer application has been leached from the soil; the main source of available nitrogen to support soil microbial growth is that associated with the crop

residue plowed back into the soil. The crop residue is mineralized by the soil microbes, i.e. decomposed and inorganic ions released. The first step of mineralization is ammonification (release of ammonium ions). These ammonium ions are then available for nitrification. These microbes can also immobilize the ammonium ions by incorporating them into their body tissue. The principal factor that determines which process occurs is the carbon-to-nitrogen (C/N) ratio of the residue being decomposed (Troeh and Thompson, 1993). Microbes use carbon both for building body tissue and as an energy source. Nitrogen is required when carbon is incorporated into body tissue. The break-even point for decomposing organic materials in a few weeks time is a C/N ratio of about 32:1, approximately that of the cotton residue. Wider ratios cause some soil nitrogen to be immobilized, and narrower ratios permit nitrification (and therefore NO emission) to occur as the organic matter decomposes (Troeh and Thompson, 1993). The soybean residue has a carbon-to-nitrogen (C/N) ratio of about 15:1, so ample nitrogen is available for production of NO by nitrification/denitrification. In contrast, the cotton and corn residue have a C/N ratio at least twice that of the soybean residue, therefore there's relatively little nitrogen (as ammonium ions) available for mineralization and subsequent NO production (Figure 7). As the soil warms up, soil microbial activity and subsequent demand for nitrogen increases. Therefore, if high C/N plant residue is the main source of available nitrogen, the amount of nitrogen available for nitrification/denitrification decreases. However, in low C/N plant residue fields, such as soybean, and to a lesser extent cotton, this increased microbial activity will foster increased nitrification over immobilization, resulting in larger NO emissions. The nitrogen carrier-based soybean (and cotton to a lesser degree) time-averaged flux levels mimic the diurnal soil temperature pattern. With soil moisture sufficient for nitrification, and adequate nitrogen available

from the residue for both immobilization and nitrification, the NO production may be driven by soil temperature, and would exhibit the trend shown here.

The mechanism by which NO release is enhanced when N<sub>2</sub> is used as the carrier gas is not well understood. One possibility is the use of a nitrogen carrier interferes with nitrogen immobilization, shifting the microbial activity toward ammonification, nitrification and subsequent NO emission. The nitrogen carrier gas may also interrupt the nitrification process before complete conversion to nitrate, allowing NO to escape. Johansson and Galbally (1984) found increased NO emissions at decreased partial pressures of O<sub>2</sub> in a laboratory experiment using a pure nitrogen atmosphere.

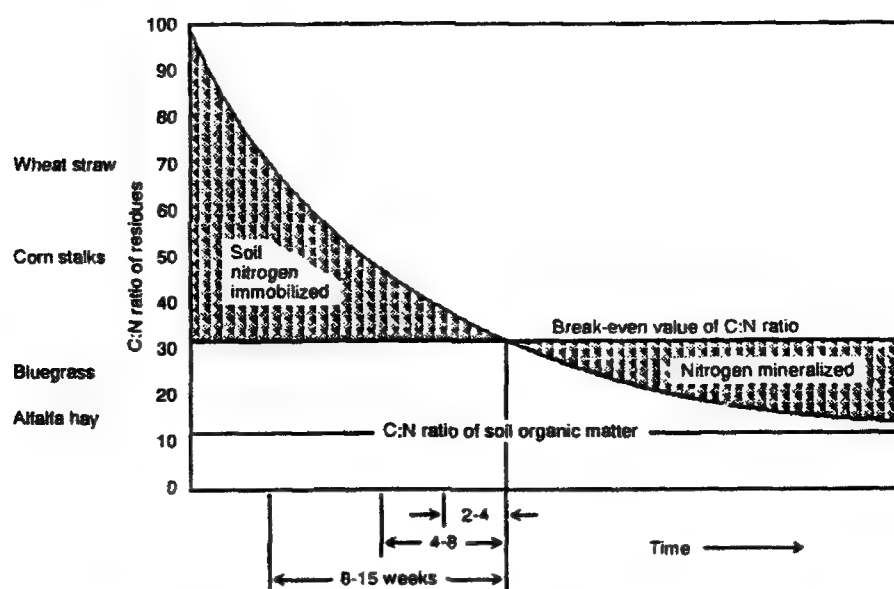


Figure 7. A schematic diagram showing the effect of C/N ratio on immobilization or mineralization of nitrogen. The time scale at the bottom indicates how much warm weather is needed for residue decomposition to begin releasing nitrogen. (Troeh and Thompson, 1993)

Another parameter that confounds the relationship of soil temperature to NO emission is soil moisture. While Williams et al. (1987) found a strong correlation

between soil temperature and soil NO emissions, they also found that soil NO emissions were significantly reduced when the soil moisture level is reduced below 10%. Anderson et al. (1988) and Johansson et al. (1988) observed (in grassland/savannah sites) a decrease in NO release rates at temperatures greater than about 35 °C. The location of this NO emission maximum also depends on soil moisture and nutrient levels (Williams and Fehsenfeld, 1991). As in the atmosphere, soil moisture and soil temperature are often inversely correlated, allowing one factor to possibly offset or dominate the other. When the soil is moist and the soil temperature is moderate, flux of NO often exhibits the exponential relationship with soil temperature described by Williams et al. (1987). However, when the soil temperature and/or soil moisture content is not optimal for biogenic processes, the relationship between these two parameters is less well-defined. When the soil moisture is low, the soil microbes thought responsible for NO production can become stressed, using the available moisture for survival rather than mineralization. As the soil moisture increases to the soils' maximum capacity, the dominant production method for NO switches from nitrification to denitrification, a much less prolific production mechanism. Additionally, under moderately wet conditions, more of the NO produced is consumed before escaping the soil. At %WFPS greater than approximately 70%, NO emission ceases (Davidson, 1991).

## SUMMARY

In the Winter/Spring 1994 measurements, the average NO flux levels varied with the C/N ratio, i.e. soybean > cotton > corn for the ambient air carrier measurements, and soybean > corn > cotton for the nitrogen carrier measurements. The NO fluxes measured using the nitrogen carrier were not significantly larger than those measured in the ambient

air carrier experiment. Therefore, other processes probably exist in field experiments not duplicated in the laboratory experiments of Johansson and Galbally (1984). However, the use of the  $N_2$  carrier did clarify the possible role of the C/N ratio in plant residue in subsequent NO emissions.

These measurements suggest that significant fluxes are generated during fallow periods when relatively low C/N ratio plant residue is mixed back into the soil, a common agricultural practice. This is supported by data reported by Slemr and Seiler (1984). In their experiments, they measured NO flux over a plant-covered (grass, clover and dandelion) soil, and then cut the plants and mixed the residue back into the soil. The resulting NO emissions from the soil mixed with plants was approximately seven times larger than that from the plant-covered location.

These results demonstrate that emission of NO from soils can be an important source of atmospheric NO concentration in the rural Southeastern US. We are currently developing a comprehensive characterization of NO flux from soils in the southeast US over several different soil types and agricultural management practices. Regardless, these preliminary results suggest agricultural management practices must be accounted for when assessing the factors affecting ambient air quality.

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### **SECTION III. A GRAPHICAL VISUALIZATION OF THE SPATIAL DISTRIBUTION OF ESTIMATED NITRIC OXIDE FLUXES FROM AGRICULTURAL SOILS IN NORTH CAROLINA WITH A COMPARISON TO LITERATURE VALUES**

#### **Abstract**

Using the assumption that the NO fluxes described in the preceding two sections are representative of those across North Carolina, these fluxes were used to develop graphical displays of the spatial distribution of soil NO emissions in the state. The visualizations have a county spatial resolution. Visualizations were developed for each crop type, during both measurement periods, using the ambient air based NO flux values. These NO emission estimates were compared to other values in the literature, (normalized to NC crop acreage). Estimates of the soil emission of NO as a percentage of total (all sources) NO emission in the state were compared to the current input values used in the Regional Oxidants Model.

## INTRODUCTION

The research described in the preceding sections provide an indication of the temporal variability of soil emissions of NO. Using the assumptions that these NO fluxes are representative of those across all soil types, environmental conditions and fertilizer application rates throughout North Carolina during the late Spring 1993 and late Winter/early Spring 1994 measurement periods, these fluxes were used to develop a graphical representation of the spatial distribution of soil NO emissions. The visualizations have a county spatial resolution. Spatial distributions were developed for each crop type, during both measurement periods, using the ambient air based NO flux values. These emissions estimates were then compared to other yearly averages in the literature (normalized to both North Carolina crop acreages and North Carolina total land area.) Finally, these estimates were compared to the current inputs to the Regional Oxidants Model (ROM) used to predict ambient ozone concentrations in the state.

## CALCULATIONS

The flux of a species *c* is defined as the mass of *c* emitted from a unit area during a unit time interval; for the data presented here the units are  $\text{ng N m}^{-2} \text{s}^{-1}$ . To generate the following inventories, the overall average NO flux values for each crop in each season (soybean/summer =  $1.8 \text{ ng N m}^{-2} \text{s}^{-1}$ , soybean/winter =  $10.2 \text{ ng N m}^{-2} \text{s}^{-1}$ , cotton/summer =  $3.8 \text{ ng N m}^{-2} \text{s}^{-1}$ , cotton/winter =  $5.1 \text{ ng N m}^{-2} \text{s}^{-1}$ , corn/summer =

8.1 ng N m<sup>-2</sup> s<sup>-1</sup>, corn/winter = 3.7 ng N m<sup>-2</sup> s<sup>-1</sup>) were converted to units of kg N/acre-year. These converted NO flux values were then multiplied by the corresponding crop acreage for each county in NC (1993 North Carolina Agricultural Statistics) to obtain the kg/year of nitrogen (as NO) emitted in that county for each combination of season and carrier gas.

Flux values from three other investigators in the literature were similarly converted and normalized by both NC crop acreage and NC total land area to assess the representativeness of the estimates. Anderson and Levine (1987) measured NO emissions from a fertilized (~ 80 kg N/acre) soil over a location near Jamestown, Virginia over a year, producing a yearly NO soil flux estimate of 2.08 Kg N/ha-yr. Johansson and Granat (1984) measured soil NO emissions in a fertilized (200 kg N/ha) field in Kjettslinge, Sweden from April to July and again in September, calculating a weighted average yearly NO emission from soil of 0.6 kg N/ha-yr. Williams et al. (1992) used a NO emissions model using soil temperature and land use type to predict NO fluxes from soil on a county spatial resolution basis for the US in January and July. An equal-weighted average of the predicted values for NC in both seasons produced an estimated flux of NO from soil of ~ 3.2 ng N m<sup>-2</sup> s<sup>-1</sup>. Each of these NO flux estimates were then multiplied by the total crop acreage (soybean = 1,349,970 acres; cotton = 460,000 acres, corn = 1,044,700 acres; 1991 data (1993 North Carolina Agricultural Statistics)) (Table 1) to provide an estimate of the source strength of NO emissions from each crop. These NO emissions estimates were also multiplied by the total NC land area (31,402,880 acres) to

estimate the source strength of NO across the entire state. All the resulting normalized NC total land area NO flux estimates were then divided by the total NO emissions from the state (anthropogenic and biogenic) to obtain the 'percent of total North Carolina (all sources) emissions of NO emitted by soils' (Table 2). The overall NC yearly estimate was computed as  $((0.60 \times \text{NC fallow field NO flux}) + (0.40 \times (0.33 \times \text{NC summer overall average NO flux}) + (0.66 \times \text{NC winter overall average NO flux})))$ . These percentage estimates were then compared to the current value used in the ROM (~ 3%).

## **SPATIAL DISTRIBUTION INVENTORY**

The combination of season and crop type allows the development of six separate inventories. Figure 1 shows the spatial distribution of soil NO emissions for the summer soybean location estimates (soybean/summer). This inventory shows the largest emissions of NO for the conditions occur in the eastern portion of NC, with yearly emissions of NO by county ranging up to ~ 25 metric ton per year. This results in a state-wide total of about 3100 metric ton per year emitted when assuming these conditions. Since the majority of agriculture in NC occurs in the eastern portion of the state, this eastern maxima is reflected in all the subsequent inventories as well.

Figure 2, the soybean/winter combination, produced the largest emission values found in any combination, with soil NO emissions approaching 143 metric ton per year in one county, producing almost 1800 metric ton per year for the state.

Figures 3 and 4 characterize the cotton location estimates. Figure 3 shows the cotton/summer emission distribution, resulting in an upper limit of ~ 21 metric ton per year for the largest emitting county, and ~ 220 metric ton per year for the state. Cotton/winter is shown in figure 4, with the upper value of soil emitted NO by county approaching 28 metric ton per year, leading to a state-wide value of ~ 370 metric ton per year.

Figures 5 and 6 reveal the distribution of soil emitted nitrogen (as NO) for the corn location combinations. The corn/summer combination is depicted in Figure 5, with the largest county emission approaching 56 metric ton per year and the combined state-wide emissions approaching 1100 metric ton per year. Finally, Figure 6 shows the corn/winter combination, with the largest corn acreage county producing ~ 25 metric ton per year, and the state producing 490 metric ton per year for these conditions.

## COMPARISON OF NO FLUX ESTIMATES TO LITERATURE VALUES

To assess the representativeness of these estimated source strengths, the NO fluxes used to produce the yearly spatial distributions were compared to yearly estimates published by other investigators (Anderson and Levine, 1987; Johansson and Granat, 1984; Williams et al., 1992) after normalization by both the actual crop acreage and total land acreage in North Carolina (1993 North Carolina Agricultural Statistics). The NO source strength estimates by crop acreage were similar (Table 1), with the weighted

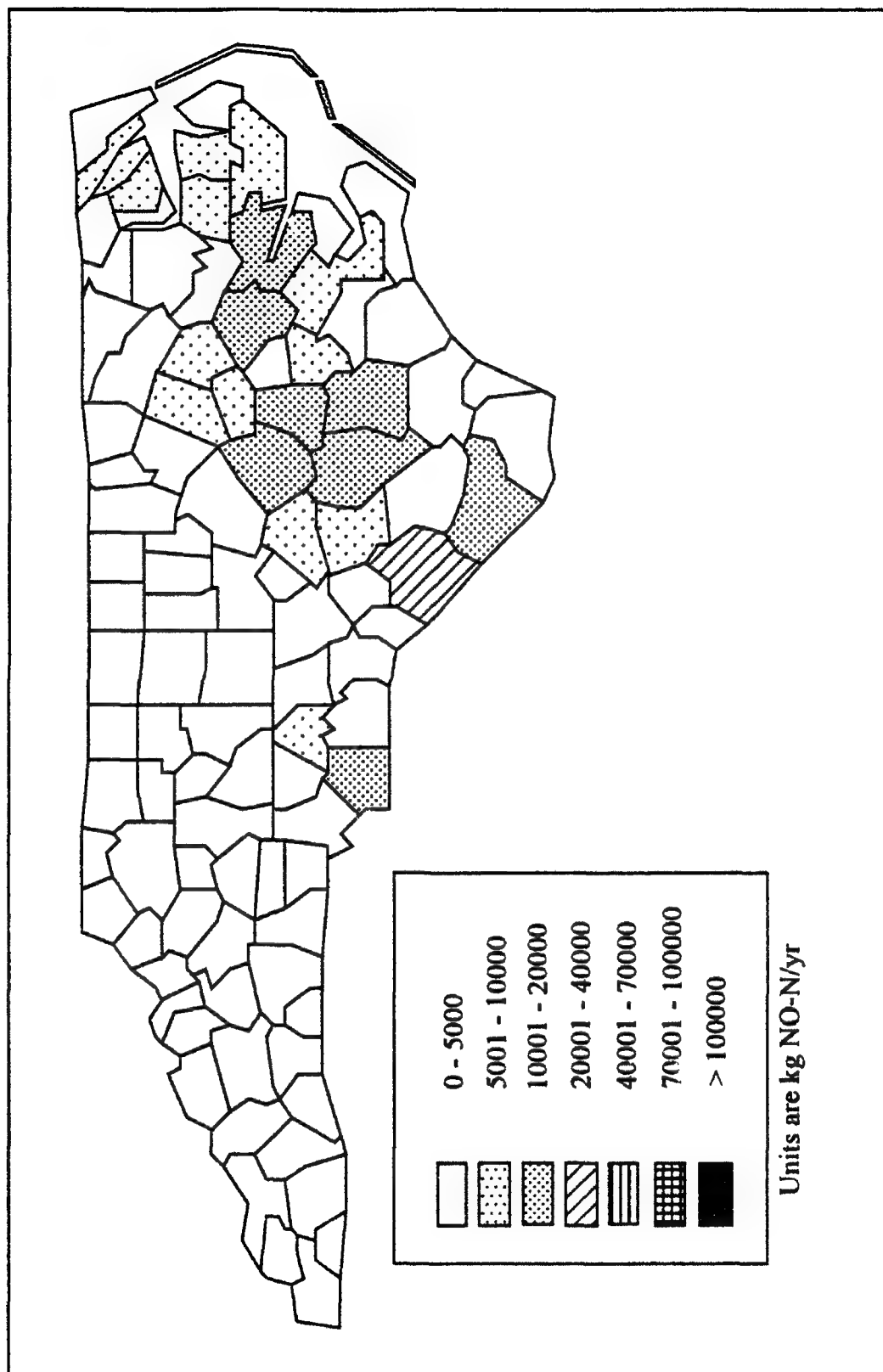


Figure 1. NO flux distribution using the Summer 1993 soybean data.

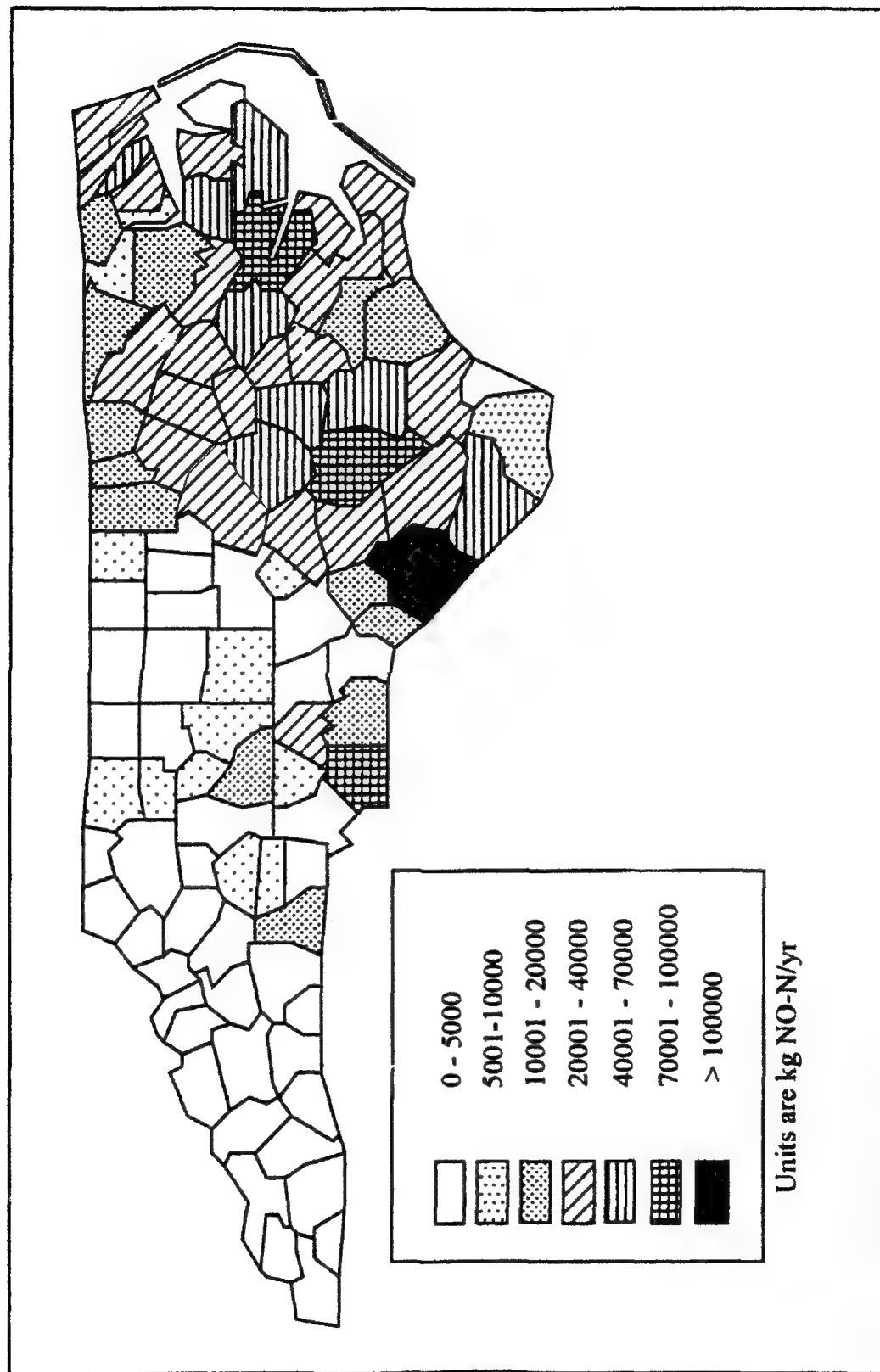


Figure 2. NO flux distribution using the Winter/Spring 1994 soybean data.

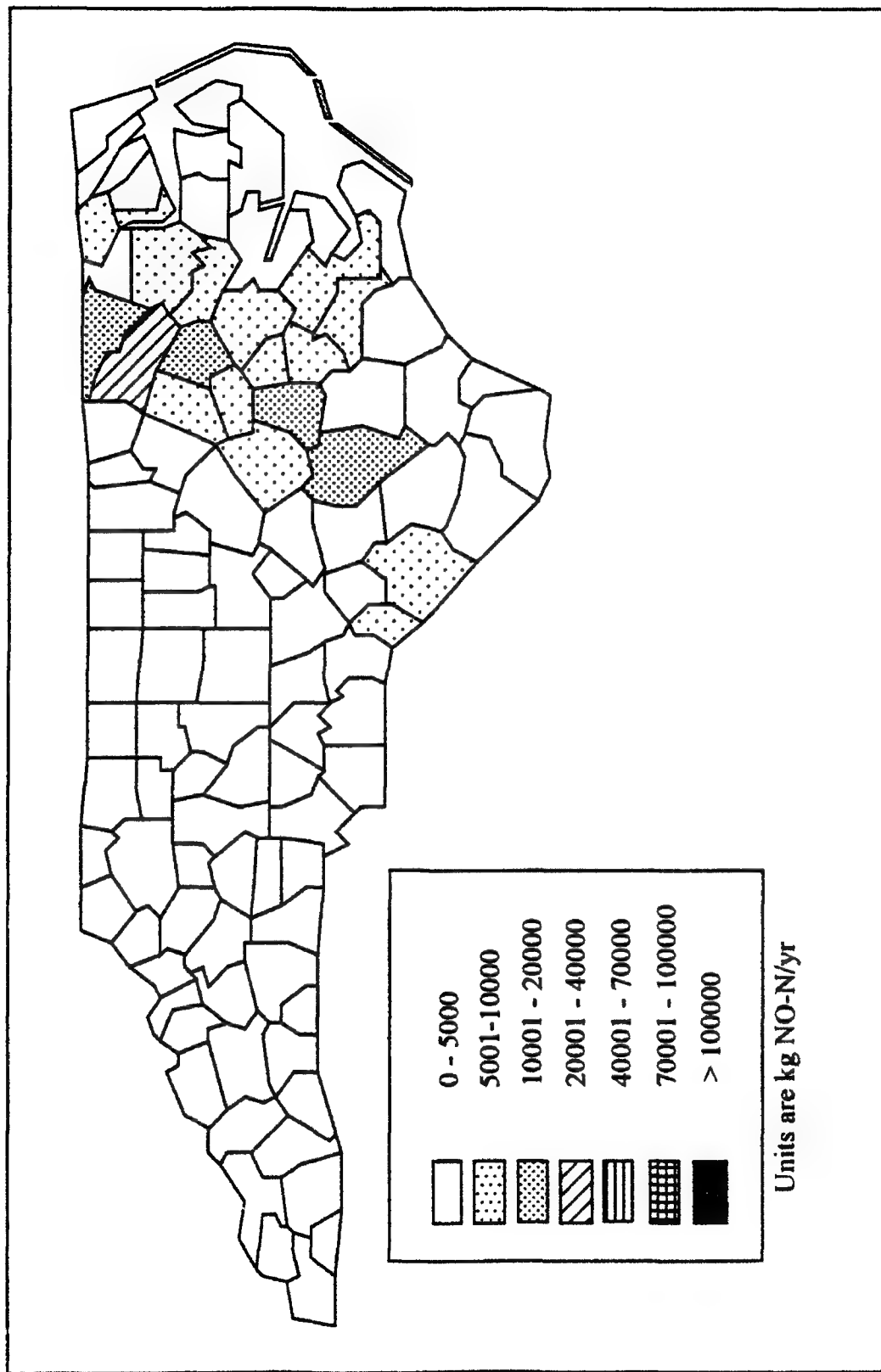


Figure 3. NO flux distribution using the Summer 1993 cotton data.



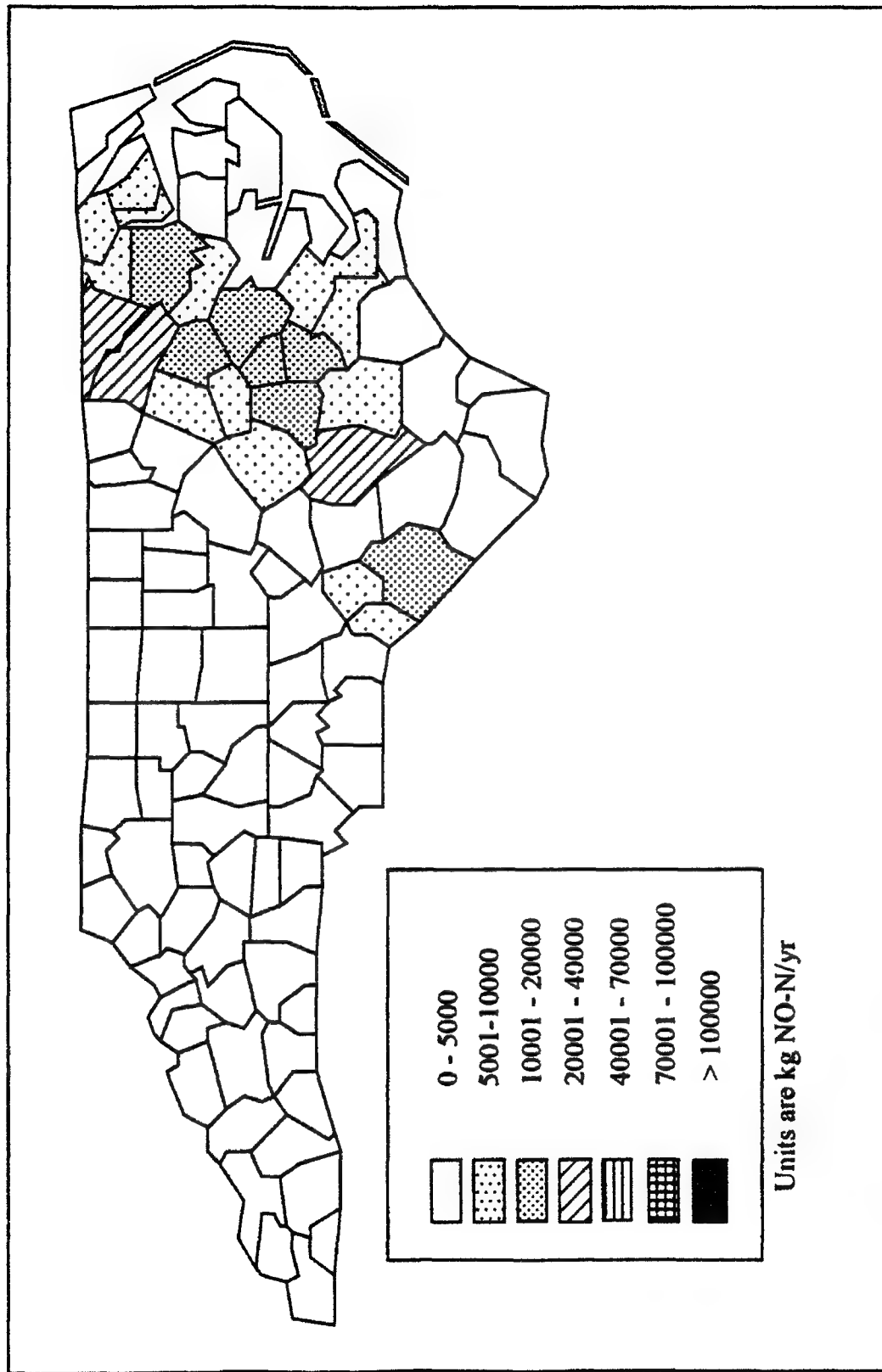


Figure 4. NO flux distribution using the Winter/Spring 1994 cotton data.

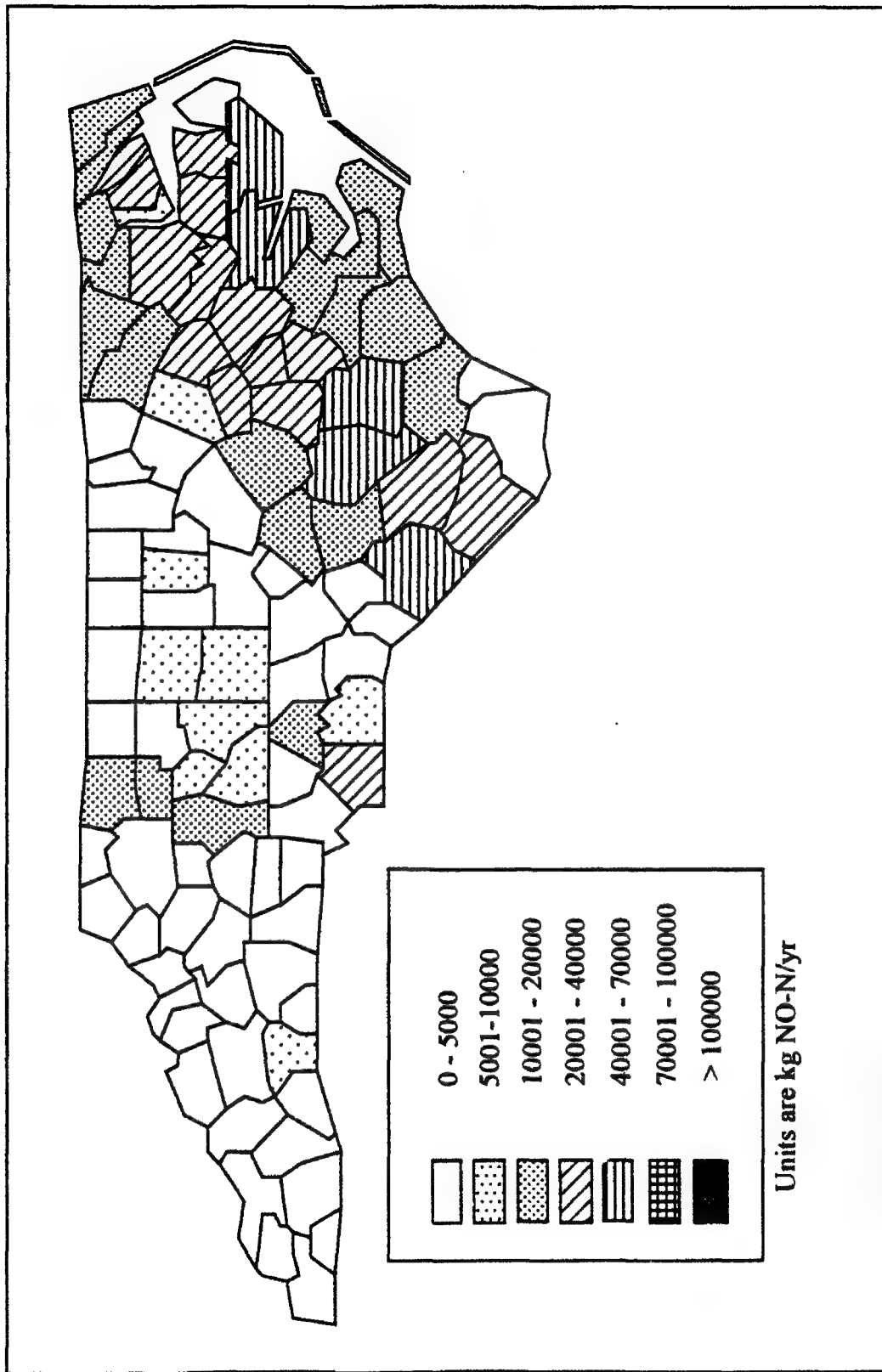


Figure 5. NO Flux distribution using the Summer 1993 corn data.

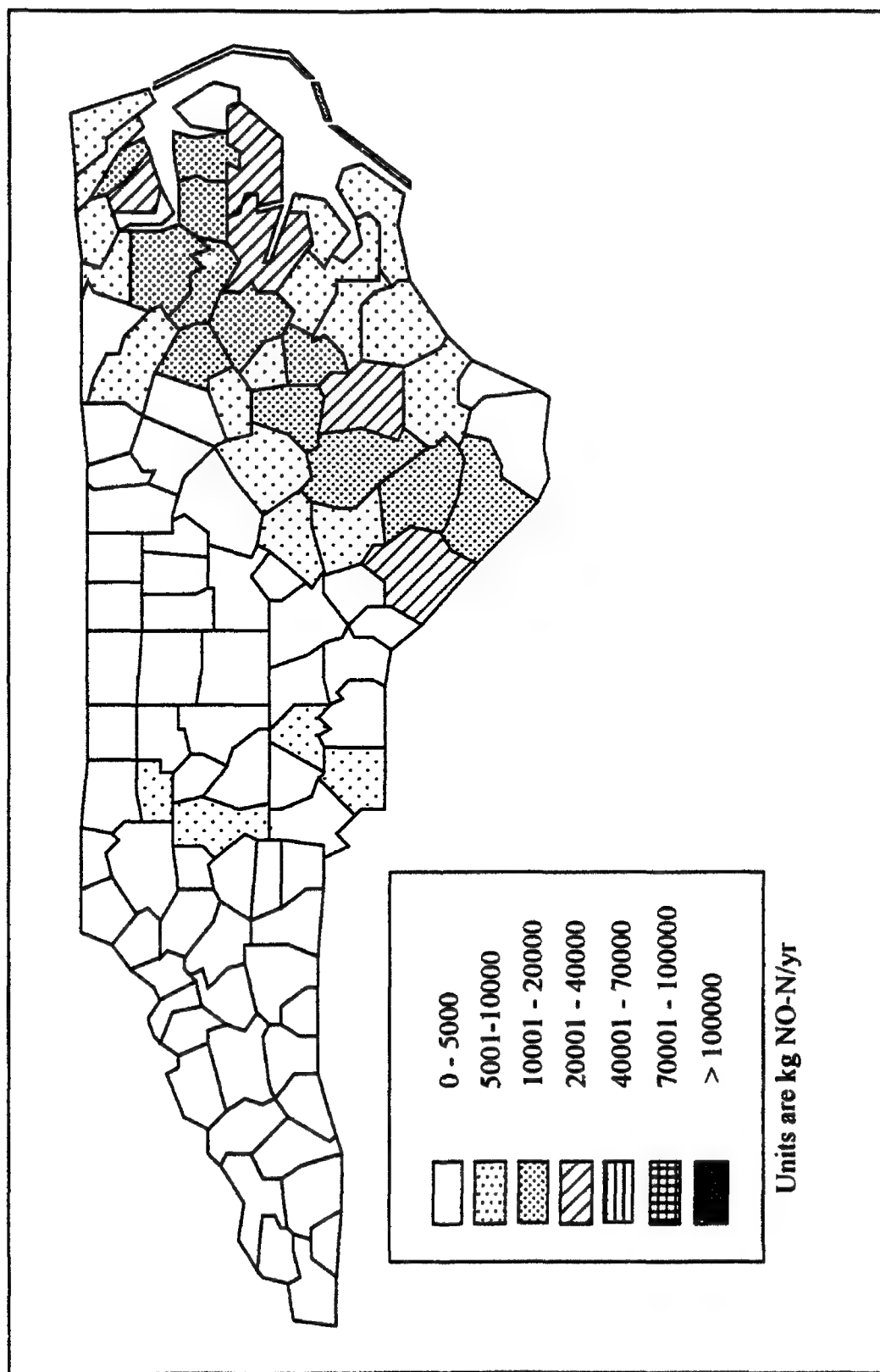


Figure 6. NO flux distribution using the Winter/Spring 1994 corn data.

Data Source	Soybean	Cotton	Corn
Holbrook, (Summer 1993) (1)	308.6	221.5	1073.9
Holbrook, (Spring 1994) (2)	1763.3	297.8	490.9
Composite NC Yearly Average (3)	1278.6	272.4	685.3
Anderson and Levine (1987) (4)	1136.7	387.3	879.6
Johansson and Granat (1984) (5)	327.8	111.7	253.7
Williams et al., (1992) (6)	551.7	188.0	426.9

NOTE: Units are metric tons of NO as N per year. Crop acreage data from 1993 North Carolina Agricultural Statistics.

- (1) - Uses 1.79 ng N/m<sup>2</sup>-s for soybean, 3.77 ng N/m<sup>2</sup>-s for cotton, and 8.05 ng N/m<sup>2</sup>-s for corn soil NO flux.
- (2) - Uses 10.23 ng N/m<sup>2</sup>-s for soybean, 5.07 ng N/m<sup>2</sup>-s for cotton, and 3.68 ng N/m<sup>2</sup>-s for corn (as previous crops) soil NO flux.
- (3) - Uses 1/3 of the Holbrook Summer 1993 NO flux by crop (1) and 2/3 of the Holbrook Spring 1994 NO flux by previous crop (2).
- (4) - Uses 2.08 kg N/ha-yr (Virginia, fertilized soil) as the soil NO flux for all three crops.
- (5) - Uses 0.6 kg N/ha-yr (Sweden, fertilized soil) as the soil NO flux for all three crops.
- (6) - Uses 3.2 ng N/m<sup>2</sup>-s as the soil NO flux for all three crops. NC statewide flux obtained from model using soil temperature and land use type as inputs. Predicted NO flux from soil applied to 1991 NC crop acreage only.

Table 1. Estimates of annual NO emissions from fertilized soil, as a function of crop, previous crop, and North Carolina total crop acreage.

average value for each crop comparing favorably to the yearly estimate for Jamestown, Virginia.

The statewide source strength estimates (Table 2) reveal the magnitude of NO emissions from North Carolina soils using several varied sources from the United States and Europe, along with output from a numerical model. In every case, the source strengths estimated here were larger than the value currently used as the input to the ROM (3 %), with the composite yearly average source strength of NO estimated for the state almost 3 times as large as the ROM input.

These inventories, while not presented as definitive, reveal the magnitude of nitrogen (as NO) possibly emitted from agriculturally-managed soils across the state of North Carolina. Agricultural enterprises are almost always rural, so fewer anthropogenic NO sources impact these locations. Therefore, the magnitude of these biogenic emissions become significant when developing effective ozone control strategies. If the soil source of NO, a biogenic precursor to ozone formation, is three times as large as the current ROM input, the potential for rural ozone formation may be underestimated.

Data source	NO emission (metric tons of N/year)	% of total NO emission (as N)
Candor, NC		
Unfertilized field (Kim et al., 1994)	7,180	4.7 %
Clayton, NC		
Agriculturally-managed fields (Holbrook, Summer 1993)	17,200	11.3 %
Clayton, NC		
Agriculturally-managed fields, fallow phase (Holbrook, Spring 1994)	24,940	16.4 %
Composite NC Yearly Average*	13,250	8.7%
Jamestown, VA		
Agricultural field, full year (Anderson and Levine, 1987)	26,440	17.4 %
Kjettslinge, Sweden		
Fertilized land, April-July, September (Johansson and Granat, 1984)	7,630	5.0 %
Model (Williams et al., 1992)	12,830	8.4 %

Total NO emissions data for NC obtained from D-S Kim, Ph.D. Dissertation, North Carolina State University, 1993.

\* NC composite yearly average calculated as 60% of NO flux measured in Candor, NC (unfertilized location) plus 40% of NO flux measured in Clayton, NC (fertilized location, NO flux averaged over a year as (1/3 of Summer 1993 + 2/3 of Spring 1994))

Table 2. Comparison of NO emissions from soil, as a percentage of total North Carolina (all sources) NO emission. All NO flux source strengths normalized to North Carolina total land acreage.

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## **APPENDICES**



## APPENDIX A

### Constants used in flux calculations

$$h = 42 \text{ cm}$$

$$V = 27 \text{ liters}$$

$$Q = 9 \text{ liters/min}$$

$$L_{\text{NO}} = 0.02 \text{ cm/sec}$$

$$L_{\text{NO}_2} = 0.08 \text{ cm/sec}$$

in R, the reaction term:

$$k_{\text{O}_3} = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$$

$$k_{\text{RO}_2} = 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$$

$$k_{\text{HO}_2} = 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$$

$$[\text{O}_3] = 5 \text{ ppbv}$$

$$[\text{RO}_2] = 18 \text{ pptv}$$

$$[\text{HO}_2] = 5.4 \text{ pptv}$$

All  $\text{NO}_x$  concentrations were measured in ppbv.

# APPENDIX B

Data from Late Summer 1993 field experiment  
Central Crops Research Station, Clayton, NC

All air temps with two decimal places (except in the overall hourly averages)  
are predicted by regression of air temp on soil temp...  
Flux units are  $\text{ng N m}^{-2} \text{ s}^{-1}$

## Soybean Crop

18-Aug-93			Temps (C)		NO input	O3(TV tower)
Hour	NO flux	NO2 Flux	Soil	Air	(ppb)	ppb
820	6.88	-25.98	24	23.4	1.6	25
850	4.77	-12.58	24.3	25	0.2	25
1020	1.73	-6.51	24.5	25.9	0	47
1105	0.51	-0.40	24.6	26.2	0.3	58
1155	0.38	0.22	25.3	30	0.17	58
1225	0.49	-0.30	25.5	31.5	0.05	60
1340	0.62	2.03	26.8	32.5	0	63
1405	0.31	0.57	26.6	31.73	0	65
1430	0.93	0.60	26.8	32.16	0	65
1505	0.31	-0.48	26.9	32.38	0	68
1535	0.93	0.86	27.1	32	0	68
1715	1.71	5.34	27.1	31.7	0.1	65
1745	0.62	2.06	27.2	31.3	0	65

19-Aug-93			Temps (C)		NO input	O3(TV tower)
	NO flux	NO2 Flux	Soil	Air	(ppb)	ppb
1330	1.42	2.37	24.8	27.84	0.1	62
1410	1.09	5.35	25.6	29.57	0.32	63
1445	0.79	0.37	26	30.43	0.1	63
1520	1.19	1.42	26.3	31.08	0.1	63
1700	1.55	0.47	27.4	33.46	0.1	51
1740	-0.32	-0.68	26.5	31.51	0.65	51
1810	2.95	-0.36	26.5	31.51	0.1	36

20-Aug-93			Temps (C)		NO input	O3(TV tower)
hour	NO flux	NO2 Flux	Soil	Air	(ppb)	ppb
1550	3.09	0.16	26.8	32.16	0	62
1630	2.15	1.69	26.9	32.38	0.05	62
1705	0.11	-1.13	27.2	33.02	0.05	62
1735	0.31	3.60	27.2	33.02	0	62
1805	0.62	1.58	27.3	33.24	0	54
1835	0.92	0.84	27.3	33.24	0	54
1900	1.54	1.90	27.4	33.46	0	47
2015	3.86	0.58	27.1	32.81	0.1	51

21-Aug-93			Temps (C)		NO input	O3(TV tower)
hour	NO flux	NO2 Flux	Soil	Air	(ppb)	ppb
1040	1.40	-1.33	23.6	25.25	0.1	56
1110	3.54	-1.17	23.9	27.8	0.15	61
1140	6.32	-1.95	24.1	29.2	0.2	61
1230	1.78	-0.53	24.7	32.8	0.05	62
1335	1.08	-1.97	25.5	31.9	0.1	63
1435	1.47	-0.34	25.9	32.2	0.05	65
1500	3.38	0.02	26.1	33.3	0	64
1525	0.32	1.01	26.2	32.8	0.1	64
1550	0.96	-2.44	26.4	30.3	0.15	64

1615	0.19	-0.31	26.5	31.7	0.08	51
1640	-1.01	4.13	26.5	31.1	0.7	51
1705	2.36	4.11	26.6	28.3	0.1	39

22-Aug-93		Temps (C)			NO input	O3(TV tower)
hour	NO flux	NO2 Flux	Soil	Air	(ppb)	ppb
740	2.58	-0.07	23.3	22.2	0.2	39
810	6.66	-3.16	23.3	22.2	0.2	45
830	2.08	0.87	23.3	23.1	0.1	45
910	5.57	-2.74	23.3	24.4	0.2	52
935	1.49	-0.18	23.3	24.4	0	52
1000	6.03	-4.08	23.5	25	0.2	56
1025	2.52	-2.63	23.5	26.1	0	56
1100	-0.70	2.14	23.7	26.7	0.8	56
1600	0.00	-0.18	26	30	0	64
1635	-0.07	0.09	26.1	30	0.05	64

Soybean data averages by hour			Temperature (C)		NO input	Ave O3
hour	NO Flux	NO2 Flux	soil	air	(ppb)	(ppb)
700	2.58	-0.07	23.30	22.20	0.20	20.8
800	5.09	-10.23	23.73	23.43	0.53	35.4
900	3.53	-1.46	23.30	24.40	0.10	47
1000	2.92	-3.63	23.78	25.56	0.08	54.8
1100	2.02	-0.24	24.32	27.98	0.32	59
1200	1.13	-0.42	25.10	32.15	0.05	59.6
1300	1.04	0.80	25.70	30.75	0.07	60.2
1400	0.92	1.25	26.18	31.22	0.09	62.2
1500	1.46	0.08	26.54	32.12	0.05	63.4
1600	0.26	1.08	26.40	31.04	0.18	61.2
1700	0.90	1.97	27.03	31.76	0.14	54.8
1800	1.49	0.70	27.03	32.66	0.03	44
1900	1.54	1.90	27.40	33.46	0.00	34
2000	3.86	0.58	27.10	32.81	0.10	37.8

Cotton Crop, air carrier, Clayton NC

(Diurnal run)

23-Aug-93

24-Aug-94

		Temps (C)			NO	O3 (TV tower)
hour	NO flux	NO2 Flux	Soil	Air	input	ppb
1050	4.26	1.43	24	31.4	0.05	49
1125	2.16	0.11	24.4	32.8	0	57
1215	1.24	1.43	24.9	32.2	0	60
1300	0.70	1.14	25.7	33.3	0.05	66
1445	0.24	1.43	27.1	34	0.05	66
1510	0.31	4.30	28	34.4	0	67
1535	1.01	4.31	28.5	33.3	0.05	67
1620	0.27	-0.52	29	31	0.2	63
1650	1.72	10.47	29.5	31	0.1	63
1730	0.46	-1.51	29.5	31.5	0	56
1805	0.31	1.64	29.5	30	0	44
1845	2.03	-2.02	29	29	0	44
1925	2.05	-13.70	29	28	0	40
2010	1.46	-6.56	28.5	23	0.2	33
2045	14.10	-27.48	28	22	0.4	33
2200	5.43	-11.09	27.5	22	0	36
2245	2.57	-5.37	27	22	0.1	36
2315	4.21	-1.61	27	22	0.07	32
2355	1.92	-1.52	26.5	21	0	32

2435	3.21	3.25	26	21	0	32
2510	2.73	-0.46	26	20	0	29
2545	1.06	-4.49	26	20	0.15	29
2625	2.26	-0.98	25.5	19	0	25
2700	0.82	-2.63	25	19	0.1	20
2735	6.98	-9.04	25	18	0.1	20
2815	9.48	-9.47	25	17.5	0.6	5
2850	10.13	-14.29	24.5	18	0.05	5
2930	8.72	-7.92	24	18	0.45	5
3005	7.95	-5.19	24	18	0.1	5
3040	7.01	-6.15	24	18	0.4	5
3115	8.55	-25.86	24	18	8.1	13
3230	38.02	-38.71	23.6	22	0.43	21
3305	0.79	-0.37	23.6	25	0	55
3350	0.94	8.64	23.9	27	0	55

24-Aug-94		Temps (C)			NO	O3
Hour	NO flux	NO2 Flux	Soil	Air	input	ppb
1210	0.23	0.09	26.3	35	0.05	62
1245	0.08	0.40	26.9	36	0.05	62
1330	0.00	-0.30	28.2	36	0	65
1410	0.16	0.31	29	38.5	0.1	68
1510	0.16	0.74	30	36	0.1	68
1540	0.39	-4.03	30.3	32	0.05	68
1610	0.51	0.95	30.3	34	0.07	70
1640	-0.07	-0.56	30.3	35.5	0.05	70
1705	0.15	-0.34	30.4	35	0	66

25-Aug-94		Temps (C)			NO	O3
	NO flux	NO2 Flux	Soil	Air	input	ppb
1705	0.31	0.51	28	34	0	68
1735	0.31	0.60	28.1	35	0	68
1800	0.32	-2.05	28.2	34	0.1	50
1830	0.39	-11.24	28.2	30.5	0.05	50
1855	0.39	-2.15	28.3	30.5	0.05	50
1920	0.17	-6.81	28.2	28.5	0.1	43
1945	0.96	-12.68	28.1	27	0.2	43
2010	3.74	-25.85	28	25	0.1	39
2035	7.44	-24.35	27.9	25	0.1	39

26-Aug-94		Temps (C)			NO	O3
	NO flux	NO2 Flux	Soil	Air	input	ppb
1300	1.01	1.76	28.6	35.7	0	62
1330	0.23	1.57	29.4	37.5	0.05	62
1400	0.60	2.33	30.2	38.7	0	65
1430	0.00	2.01	31	38.5	0	65
1500	0.00	0.40	31.8	39	0	57
1600	0.31	-2.26	32.5	33.5	0	52
1640	0.32	-1.82	32.5	25	0	52
1705	0.63	-5.18	32.5	24.7	0	40
1740	0.00	-6.96	32	25	0	40
1815	2.38	-26.14	31.4	25	0.1	20
1900	7.84	-24.46	30.7	25	0.8	13

28-Aug-94		Temps (C)			NO	O3
	NO flux	NO2 Flux	Soil	Air	input	ppb
730	16.79	-12.32	24.9	22	2.25	5
800	13.53	-9.38	24.8	23	1.62	12
835	12.36	-11.13	24.9	25	3	12
905	15.24	-9.80	25	26	1	24
930	9.30	-8.93	25.1	28	2	24

1000	9.52	-6.15	25.4	30.7	0.5	42
1035	6.08	-5.43	25.8	32	0.2	42
1105	3.27	-3.30	26.4	33	0.3	53
1130	1.46	-0.69	26.7	35.3	0.05	53

Cotton data averages by hour			Temperature (C)		NO input	Ave O3
hour	NO Flux	NO2 Flux	soil	air	(ppb)	(ppb)
0	3.21	3.25	26.00	21.00	0.00	21.8
100	1.90	-2.47	26.00	20.00	0.08	18.4
200	2.26	-0.98	25.50	19.00	0.00	15.3
300	3.89	-5.83	25.00	18.50	0.10	12.2
400	9.80	-11.88	24.75	17.75	0.33	8.4
500	8.72	-7.92	24.00	18.00	0.45	6
600	7.48	-5.67	24.00	18.00	0.25	5
700	12.70	6.73	24.45	20.00	5.18	13
800	21.26	-19.61	24.43	23.33	1.68	20.5
900	6.58	-2.61	24.40	26.50	0.75	40.2
1000	6.62	-3.38	25.07	31.37	0.25	50
1100	2.29	-1.29	25.83	33.70	0.12	58.4
1200	0.51	0.64	26.03	34.40	0.03	60.2
1300	0.48	1.04	27.98	35.63	0.03	62.6
1400	0.25	1.52	29.33	37.43	0.04	65
1500	0.37	1.27	29.72	34.94	0.04	64.4
1600	0.51	1.05	30.68	31.67	0.07	62.8
1700	0.31	-2.10	30.08	30.87	0.00	55.4
1800	0.97	-6.91	29.10	29.83	0.05	39.4
1900	2.74	-14.36	29.00	26.63	0.28	34.6
2000	6.68	-21.06	28.10	23.75	0.20	32.8
2100			no data this hour			
2200	4.00	-8.23	27.25	22.00	0.05	25
2300	3.07	-1.56	26.75	21.50	0.04	20.2

Corn Crop at Clayton, NC  
Central Crops Research Station  
Ambient air as the carrier

29-Aug-93			Temps (C)		NO data	O3 (TV tower)
hour	NO flux	NO2 Flux	Soil	Air	input	ppb
1550	10.33	17.82	31.8	37.5	0.1	69
1620	9.69	17.20	32	38	0.05	64

30-Aug-93			Temps (C)		NO data	O3 (TV tower)
hour	NO flux	NO2 Flux	Soil	Air	input	ppb
800	52.79	-30.27	25.1	24	1	24
835	45.08	-20.63		25	0.1	24
900	36.15	-11.07		27.5	0.25	39
930	33.13	-7.41		29	0.4	39
1000	32.63	-2.91		30.5	0.2	54
1030	23.30	5.80		32.5	0.1	54
1145	10.62	20.02		37.5	0	68
1215	8.44	20.67		37	0.05	69
1250	10.94	20.90		37.25	0	69
1320	11.21	22.20		38	0	73
1345	5.00	23.46		39	0.1	73
1415	7.13	24.68		38	0.1	75
1450	3.21	28.81		36	0.1	75

1520	2.42	28.52	38	0	67
1600	8.45	29.18	34	0.1	66
1615	5.18	26.92	32	0.05	66
1645	9.01	27.78	36	0.1	66
1725	5.05	22.46	35	0.02	68
1745	6.75	25.13	34	0	68

31-Aug-93			Temps (C)		NO data	O3 (TV tower)
hour	NO flux	NO2 Flux	Soil	Air	input	ppb
1420	0.12	1.38		35	0	43
1500	0.61	-0.25		35	0	48
1530	1.22	0.36		36	0	48
1555	3.06	-1.04		35	0	48
1620	0.37	0.54		35	0.15	50
1645	0.01	0.64		34	0.1	50
1710	0.00	0.30		34	0	52
1745	0.31	0.17		33	0	52
1805	0.00	0.02		32	0	38
1830	0.00	-0.08		31	0	38

1-Sep-93			Temps (C)		NO data	O3 (TV tower)
hour	NO flux	NO2 Flux	Soil	Air	input	ppb
1005	1.10	-0.63		31	0.1	72
1030	0.32	0.96		33	0.1	72
1100	-0.54	0.79		34	0.7	84
1200	0.30	0.56		38	0	90
1225	0.38	-0.34		37.5	0.05	90
1250	0.31	-1.15		39	0.1	90
1315	0.01	-0.10		39	0.1	79
1340	0.72	-0.46		39	0.05	79
1405	0.16	0.06		39	0.1	73
1430	0.23	0.15		39.5	0.05	73
1455	0.08	-5.70		40	0.15	73
1515	0.99	-0.70		39	0.05	71

Corn data averages by hour			Temperature (C)		NO input	Ave O3
hour	NO Flux	NO2 Flux	soil	air	(ppb)	(ppb)
800	48.93	-25.44	25.1	24.5	0.55	27
900	34.63	-9.23		28.25	0.325	40.5
1000	14.32	1.08		31.75	0.125	53.25
1100	5.08	10.50		35.75	0.35	62.25
1200	4.07	8.18		37.8	0.04	65.75
1300	4.23	11.34		38.75	0.0625	65.25
1400	1.82	8.28		38.67	0.083333	65
1500	3.11	7.55	31.8	36.75	0.025	63.75
1600	5.46	17.13	32	34.83	0.091667	62.75
1700	3.03	12.13		34	0.005	59.75
1800	0.00	-0.03		31.5	0	44

#### NO Flux-Hourly Averages/Standard Deviations

flux units are  $\text{ng N m}^{-2} \text{s}^{-1}$

Data gathered at Clayton NC (Central Crops Research Station)

from Aug 18 to Sep 1 1993

Hour (EST)	Soybean NO Flux	Soybean NO sdev	Cotton NO Flux	Cotton NO Sdev	Corn NO Flux	Corn NO sdev
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700	2.58		12.67	5.83		
800	5.09	2.22	21.30	14.49	48.94	5.45
900	3.53	2.88	6.57	7.02	34.64	2.13
1000	2.92	2.13	6.62	2.67	14.34	16.20
1100	2.01	2.88	2.29	0.91	5.04	7.89
1200	1.13	0.91	0.52	0.63	4.07	5.20
1300	1.04	0.40	0.48	0.45	4.23	5.15
1400	0.92	0.43	0.25	0.26	1.83	2.87
1500	1.45	1.26	0.37	0.38	3.11	3.66
1600	0.25	1.16	0.51	0.62	5.45	4.36
1700	0.91	0.98	0.31	0.22	3.03	3.39
1800	1.50	1.27	0.97	0.96	0.00	0.00
1900	1.54		2.76	3.48		
2000	3.86		6.69	5.53		
2100						
2200			4.00	2.03		
2300			3.07	1.62		
2400			3.21			
2500			1.90	1.18		
2600			2.26			
2700			3.90	4.35		
2800			9.80	0.46		
2900			8.72			
3000			7.48	0.66		

NO<sub>2</sub> Flux-Hourly Averages/Standard Deviations

flux units are ng N m<sup>-2</sup> s<sup>-1</sup>

Data gathered at Clayton NC (Central Crops Research Station)

from Aug 18 to Sep 1 1993

Hour (EST)	Soybean NO <sub>2</sub> Flux	Soybean NO <sub>2</sub> sdev	Cotton NO <sub>2</sub> Flux	Cotton NO <sub>2</sub> sdev	Corn NO <sub>2</sub> Flux	Corn NO <sub>2</sub> sdev
700	-0.07		6.77	26.99		
800	-10.21	11.93	-19.74	16.45	-25.45	6.82
900	-1.46	1.81	-2.62	8.62	-9.24	2.59
1000	-3.63	2.22	-3.38	4.18	1.05	4.15
1100	-0.23	1.56	-1.30	1.78	10.41	13.60
1200	-0.42	0.17	0.64	0.70	8.13	11.57
1300	0.81	2.41	1.04	0.93	11.27	13.35
1400	1.25	2.31	1.52	0.89	8.23	14.61
1500	0.06	1.28	1.27	3.59	7.45	12.65
1600	1.08	1.88	1.04	4.75	17.04	13.43
1700	1.98	2.48	-2.15	3.18	12.02	13.64
1800	0.69	0.97	-6.99	10.31	-0.03	0.07
1900	1.90		-14.41	7.35		
2000	0.58		-21.06	9.75		
2100						
2200			-8.23	4.05		
2300			-1.56	0.07		
2400			3.25			
2500			-2.47	2.85		
2600			-0.98			
2700			-5.84	4.53		
2800			-11.88	3.40		
2900			-7.92			
3000			-5.67	0.68		

Subtract 2400 from hour > 2400

# APPENDIX C

Winter/Spring NOx measurements, Central Crops Research Station, Clayton NC.

Crop designations are by previous crop in that location

Flux units are ng N/m<sup>2</sup>-s, temperatures are in degrees C

## Soybean measurements

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
7-Feb-94	1100	10.2	12.3	2.31	-9.83	0.42	2.02
Soy 1	1200	12.5	13.8	13.15	-22.94	0.00	0.00
	1300	14.2	15.2	8.18	-27.05	0.08	0.00
	1400	14.2	15.2	-3.22	-14.45	0.20	0.00
	1500	14.1	15.7	3.92	-2.18	0.00	0.00
	1600	12.5	16.3	2.28	7.74	0.00	0.00
	1700	11	15	0.00	-3.00	0.08	0.00
	1800	10.1	11.6	0.00	10.67	0.00	0.00
	Ave	12.35	14.39	3.33	-7.63	0.10	0.25
	Std Dev	1.75	1.67	5.17	13.55	0.15	0.71
Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
8-Feb-94	800	8.1	12.5	1.65	0.40	0.66	0.00
Soy 2	900	9.1	13.1	3.95	-1.78	0.17	0.00
	1000	9.6	13.6	3.62	-2.51	0.00	0.00
	1100	11.5	16.1	2.61	-2.31	0.33	0.00
	1200	11.8	16	0.65	-2.73	0.82	0.00
	1300	11.6	15.1	0.49	-3.24	1.48	0.00
	Ave	10.28	14.40	2.16	-2.03	0.58	0.00
	Std Dev	1.56	1.54	1.47	1.28	0.54	0.00
Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
14-Feb-94	900	0.9	5	26.52	-34.58	1.88	3.31
Soy 2	1000	1.7	6	28.53	-41.28	0.00	1.65
Again...	1100	4	8.1	6.71	-27.64	0.00	0.00
	1200	6.3	9	8.69	-23.78	0.00	0.00
	1300	8	10.5	7.65	-18.38	0.33	0.20
	1400	9	11.6	4.31	-23.97	0.33	0.20
	1500	9.2	12.2	2.97	-12.49	0.17	0.20
	1600	8.8	11.8	0.00	-23.66	0.00	0.00
	1700	8.1	11.1	1.00	-21.89	0.00	0.00
	1800	7	8.2	-4.21	-55.13	0.00	2.05
	1900	6.1	4.6	45.51	-88.63	0.00	0.00
	2000	5.5	3.5	133.06	-141.04	0.69	0.00
	Ave	6.22	8.47	21.73	-42.71	0.28	0.63
	Std Dev	2.78	3.08	37.96	37.22	0.55	1.09
Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
15-Feb-94	700	1.2	0.5	5.86	-74.53	1.91	0.00
Soy 3	800	1.5	1.9	75.90	-68.19	3.11	0.00
	900	2	4.3	39.55	-52.33	3.77	0.00
	No 1000..	6.3	12	18.52	-28.38	0.67	0.00
	1200	7.7	13.2	15.81	-27.18	5.80	0.00
	1300	9.8	16.1	7.82	-16.64	7.06	0.00
	1400	10.1	15.2	5.56	-13.52	4.61	0.00 84



Continue 16-Feb-94 Soy 3	1500	10	15.6	3.27	-21.51	15.30	0.00
	1600	9.5	14.5	2.95	-19.94	16.01	0.00
	1700	9.3	13.8	1.31	-9.51	12.25	0.00
	1800	8.5	10.6	1.00	-9.21	21.25	0.00
	1900	7.3	5.9	11.54	-33.90	22.46	0.00
	2000	6.5	4.5	-10.77	-37.21	18.47	0.00
Ave		6.90	9.85	13.72	-31.70	10.21	0.00
Std Dev		3.30	5.63	22.12	21.32	7.73	0.00

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
17-Feb-94 Soy 4	600	2.1	0	-0.33	5.60	0.87	0.00
	700	2	0.2	22.42	4.44	1.74	0.00
	800	2.1	2.5	21.27	-14.92	5.17	0.00
	900	2.8	6.9	8.29	-7.49	6.78	0.00
	1000	3.6	9.3	11.20	-6.59	18.83	0.00
	1100	6	12.2	7.60	-1.92	33.12	0.00
	1200	8.7	13.7	4.27	-6.63	43.71	0.00
	1300	10.5	15	5.26	-9.03	48.29	0.20
	1400	12.1	16	3.26	-6.60	52.23	0.00
	1500	12.8	17.6	1.62	-3.28	42.63	0.00
	1600	11.6	16.6	2.50		19.83	0.20
	1700	11	14.3	62.25	-37.70	19.82	0.20
	1800	9.5	11.4	3.21	27.60	12.85	0.20
	1900	8.6	8.7	2.41	-30.96	9.27	0.20
	2000	7.8	5.9	44.45	-41.45	6.13	0.41
	Ave	7.41	10.02	13.31	-9.21	21.42	0.09
	Std Dev	3.98	5.87	17.89	18.04	17.95	0.13

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
4/5-mar-94 Soy 5 Diurnal	600	2.7	5	3.57	7.58	2.39	0.41
	700	3.3	10.8	7.67	-22.63	5.02	1.22
	800	4.8	15.6	5.58	-10.69	2.96	0.60
	900	6.3	14.3	6.94	-2.01	7.10	1.00
	1000	7.5	16.5	5.53	0.58	11.31	0.99
	1100	10.1	19.3	4.86	-5.32	27.12	1.77
	1200	12.1	21.3	4.66	-8.22	31.29	1.76
	1300	12.3	23	2.87	2.47	31.59	2.33
	1400	13.7	23.9	2.39		19.18	0.00
	1500	14.1	23.6	2.08	-8.30	10.88	4.85
	1600	13.8	23.9	1.29	-6.05	8.31	2.91
	1700	13.1	23.7	0.95	-1.57	8.80	2.72
	1800	12	18.5	0.32	-4.83	8.30	1.58
	1900	11	15.5	0.83	9.94	10.69	2.00
	2000	10.3	13.6	0.33	26.01	9.27	1.61
	2100	9.6	12	0.51	-8.81	9.16	1.62
	2200	9.2	11.3	2.34	1.58	7.51	2.02
	2300	8.7	10.1	10.17	23.92	7.38	2.44
	2400	8.4	10	40.99	38.45	7.38	5.49
	subtract > 2400...	8	10.1	9.01	17.08	6.71	9.56
	2500	7.7	10.2	0.69	4.53	6.03	4.47
	2700	7.3	8.5	3.91	-0.33	5.90	2.25
	2800	6.9	7.9	0.36	0.54	5.07	1.23
	2900	6.7	7	0.85	-0.78	5.42	1.23
	Ave	9.15	14.82	4.99	2.31	10.62	2.34
	Std Dev	3.23	6.04	8.21	13.52	8.20	2.04

Start Cotton field data, same location as above.

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
1-Mar-94	600	3.8	4	-11.71	-53.30	1.03	0.42
Cotton 1	700	3.9	3.2	4.14	-37.62	1.37	0.42
	800	3.9	3.6	10.66	1.01	1.20	0.21
	900	4	3	5.04	-4.74	1.72	0.00
	1000	4.2	2.5	10.50	15.11	3.96	0.00
	1100	4.3	3.3	8.94	-3.54	3.95	0.00
	1200	4.8	3.8	3.43	-0.57	6.69	0.00
	1300	5	4.2	3.24	-1.09	10.79	0.00
	1400	5.1	4.1	1.57	-5.28	17.81	0.21
	1500	5	3.7	1.39	0.99	10.64	0.21
	1600	5	3.5	2.73	-1.40	19.05	0.00
	1700	4.7	3.1	1.02	0.22	15.13	0.00
	1800	4.5	3.5	0.52	1.25	12.53	
	1900	4.3	3.2	0.52	2.91	12.03	0.00
	2000	4.1	3	3.10	2.72	11.69	0.00
	Ave	4.44	3.45	3.01	-5.56	8.64	0.10
	Std Dev	0.46	0.47	5.30	17.13	6.22	0.16

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
3-Mar-94	600	3.5	1.7	17.69	2.01	4.49	0.21
Cotton 2	700	3.4	1.8	7.80	-6.58	0.86	0.42
	800	3.3	2.1	19.72	-0.62	1.04	0.00
	900	4	3.3	14.95	-20.77	1.37	0.00
	1000	5	4.2	18.01	-23.75	1.20	0.00
	1100	5	4.6	14.20	-14.42	0.85	0.00
	1200	4.9	4.8	8.89	-11.10	0.85	0.00
	1300	5	5.4	8.54	-12.60	0.68	0.00
	1400	5.6	6.6	5.47	-7.78	1.53	0.00
	1500	6.7	7.1	2.92	-12.70	0.85	0.00
	1600	6.3	7.8	2.19	-4.65	0.85	0.00
	1700	6.2	8.1	1.19	1.07	0.34	0.00
	1800	5.8	7.2	-0.11	0.14	2.20	0.21
	1900	5.2	6.3	0.70	3.10	4.25	2.06
	2000	5	6.7	0.70	11.65	5.60	0.21
	2100	4.6	6.1	0.72	2.87	5.61	0.00
	2200	4.3	6	1.04	1.41	5.44	0.21
	Ave	4.93	5.28	7.33	-5.45	2.24	0.19
	Std Dev	1.01	2.06	7.06	9.45	1.96	0.50

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
7-Mar-94	700	7.8	8.2	109.55	-63.49	3.21	1.02
Cotton 3	800	8.3	10.2	19.24	-24.84	4.53	0.61
	900	9.9	14.1	18.45	-10.19	6.28	0.00
	1000	13.2	21.2	6.90	-6.34	30.17	3.91
	1100	13.9	24.3	5.73	-6.84	39.27	2.32
	1200	17.7	28.2	4.43	-6.11	6.30	1.72
	1300	18	26.2	2.57	-2.98	5.24	0.38
	1400	17.6	27.6	1.88	-2.96	2.68	0.00
	1500	17.8	26.8	1.11	-2.40	2.85	0.00
	1600	17.8	27.8	1.42	-9.55	3.63	0.00
	1700	17.3	27	1.26	-3.05	4.43	0.00
	1800	16.3	22	1.60	-0.84	7.08	0.00
	1900	15.2	18.7	0.65	-1.56	8.95	0.00
	2000	14.8	17.4	0.17	1.87	8.99	0.00

Ave	14.69	21.41	12.50	-9.95	9.54	0.71
Std Dev	3.63	6.76	28.61	16.69	11.00	1.18

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
8-Mar-94	600	13.2	13.6	1.01	-1.93	1.16	0.20
Cotton 4	700	13.3	14.7	2.29	6.38	4.62	0.40
	800	13.7	16.7	5.55	-9.29	5.73	0.40
	900	14.8	20.1	3.73	-8.04	2.11	0.20
	1000	15.9	25.1	4.60	-6.81	7.01	0.97
	1100	16.3	27.8	3.16	-3.59	16.41	1.34
	1200	18.2	30.1	6.86	-4.04	6.58	1.33
	1300	20.1	31.5	2.33	-2.74	2.49	0.76
	1400	21	31.2	1.26	-1.27	1.72	0.57
	1500	20.1	28.3	0.94	-0.78	1.42	0.19
	1600	18.8	28	1.57	-2.86	1.10	0.00
	1700	18.2	27	0.94	-2.68	2.06	0.00
	1800	17.6	23.6	0.66	-6.18	4.64	0.19
	1900	16.6	20.3	0.00	4.38	2.91	0.20
	2000	16.1	19.8	0.52	0.03	2.92	0.20
	Ave	16.93	23.85	2.36	-2.63	4.19	0.46
	Std Dev	2.51	5.97	2.03	4.23	3.90	0.44

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
18-Mar-94	600	6.2	6.3	2.36	-9.18	23.11	0.21
Cotton 5	700	6.6	7.8	4.72	-6.65	42.43	0.41
Diurnal	800	6.9	8.4	4.89	-9.99	38.96	0.41
	900	7.5	10	4.00	-11.31	28.68	0.41
	1000	9.2	16.1	7.85	-16.35	12.31	1.00
	1100	11.9	20.9	5.47	-3.23	2.75	0.39
	1200	13	22.7	3.06	-11.22	1.44	0.39
	1300	11	14.5	4.44	-19.77	0.99	0.20
	1400	11.8	20.4	4.67	0.07	0.81	0.20
	1500	12.6	18.6	2.26	-0.45	0.65	0.20
	1600	13.2	19.7	2.60	-3.63	0.65	0.39
	1700	13.2	20.2	0.05	-4.01	0.49	0.20
	1800	12.5	16.6	-0.30	-23.16	0.49	0.99
	1900	12	16	0.35	3.37	0.66	0.40
	2000	11.3	11.7	0.33	-15.79	0.67	2.22
	2100	10.5	9.7	1.51	-11.55	1.18	2.24
	2200	9.7	9.8	0.36	-5.82	1.01	0.20
	2300	9.2	11.6	-0.31	1.14	1.00	0.61
	2400	9	12	1.02	-1.67	0.83	0.00
	2500	8.8	11.6	0.51	-1.29	1.50	0.00
	2600	8.7	10.9	0.69	-1.62	0.84	0.00
	2700	8.9	10.8	-0.28	-0.95	1.17	0.20
	2800	8.5	10	0.02	-0.64	1.17	0.20
	2900	8.2	8.8	0.23	0.99	0.67	0.20
	Ave	10.02	13.55	2.10	-6.36	6.85	0.49
	Std Dev	2.19	4.81	2.29	7.17	12.72	0.59

Start Corn readings

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
16-Mar-94	600	8	7.1	0.34	-10.25	1.19	0.41

Corn 1 Diurnal	700	8.1	11.5	5.81	-12.52	14.35	0.00
	800	8.3	10.8	4.50	-12.38	19.90	0.20
	900	9	13.3	3.82	-10.08	9.78	0.20
	1000	10.4	16.6	3.28	-5.30	0.98	0.20
	1100	13	18.7	40.39	6.14	0.49	0.20
	1200	13.6	16.2	3.26	-7.48	0.66	0.20
	1300	13.2	18.7	3.55	-6.17	0.16	0.20
	1400	14.7	17.7	2.59	-6.35	0.16	0.20
	1500	14.1	21.3	1.62	-4.82	0.48	0.00
	1600	13.6	21.2	1.60	-5.10	0.48	0.20
	1700	12.1	20.1	0.64	-18.58	1.30	0.00
	1800	10	11.5	0.00	-9.28	3.34	0.00
	1900	9.1	7.5	-0.16	-7.56	1.02	0.00
	2000	8.5	6.1	-0.31	-5.82	0.51	0.00
	2100	7.6	4.7	-0.16	-4.36	0.68	0.00
	2200	7	3.8	0.00	-4.12	0.34	0.00
	2300	6.2	2.3	0.34	-3.86	0.17	0.21
	2400	5.8	0.9	0.00	-3.47	0.00	0.00
	2500	5.5	-0.3	0.00	-44.27	0.17	0.21
	2600	5.2	-1.2	-17.51	-64.55	0.00	0.42
	2700	5.1	-0.4	0.35	-4.99	0.17	0.21
	2800	4.5	-1.5	1.04	-3.62	0.17	0.42
	2900	4.1	-1.2	0.00	-1.01	0.17	0.21
	Ave	9.03	9.39	2.29	-10.41	2.36	0.15
	Std Dev	3.36	8.05	9.16	14.62	5.03	0.14

Day 17-Mar-94 Corn 2	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
	600	3.3	0	2.26	-3.46	17.56	1.90
	700	3.7	5	6.70	-15.52	24.07	0.21
	800	4.3	10.2	10.19	-10.39	20.28	0.20
	900	4.7	10	10.66	-10.67	15.77	0.41
	1000	6.8	13.2	5.45	-7.41	6.80	0.60
	1100	8.3	13	4.18	-7.84	3.82	0.60
	1200	11.2	15.5	5.23	-8.13	0.82	0.40
	1300	12.3	18.3	4.30	-49.98	0.65	0.20
	1400	12.7	18.7	6.83	-19.04	0.81	0.20
	1500	12.7	18.7	3.55	-2.11	0.65	0.20
	1600	12	18	7.45	7.85	2.61	0.40
	1700	10.9	17.7	1.95	-9.55	0.65	0.20
	1800	9.6	10.8	1.33	-11.57	0.84	0.20
	1900	8.7	6.4	3.26	-7.22	1.02	0.41
	2000	8.1	4	3.95	-29.20	1.03	0.21
	Ave	8.62	11.97	5.15	-12.28	6.49	0.42
	Std Dev	3.39	6.03	2.79	13.23	8.40	0.43

Day 22-Mar-94 Corn 3	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
	600	10.6	11.7	1.83	-8.49	23.34	3.44
	700	10.8	12.6	3.30	-7.13	32.57	1.01
	800	11.5	14.2	8.53	-11.06	37.68	1.00
	900	13	18.6	8.90	-13.34	25.23	0.79
	1000	14.7	19.8	6.29	-4.48	12.00	1.57
	1100	16.2	22.4	4.00	-3.21	1.93	0.58
	1200	16.8	23.7	3.35	-2.06	1.44	0.39
	1300	17.5	26.6	4.89	-7.90	0.95	0.38
	1400	17.6	25.1	3.48	-4.22	0.96	0.39
	1500	17	25.6	3.16	-8.13	0.64	0.58

1600	15.3	23.8	2.73	-1.67	0.80	0.39
1700	14.6	23.3	1.59	-8.58	1.28	0.19
1800	13.7	20	1.93	-9.13	1.46	0.39
1900	12.8	14.5	5.61	25.33	2.48	1.20
2000	12	12.4	-8.53	-7.52	2.33	2.62
Ave	14.27	19.62	3.40	-4.77	9.67	1.00
Std Dev	2.43	5.28	3.99	8.94	13.17	0.92

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
23-Mar-94 Corn 4	600	9.3	7.8	17.03	-3.58	24.85	2.46
	700	9.7	16	14.40	-7.50	36.79	2.19
	800	10.6	20	10.62	-14.98	12.47	1.96
	900	11.3	22.3	13.30	-28.70	7.88	1.95
	1000	11.8	23.2	8.30	-9.52	5.93	1.75
	1100	13.4	27.2	4.71	-9.78	2.06	1.15
	1200	16.8	29.5	5.30	-3.72	0.94	0.95
	1300	17.8	29.7	3.11	-5.16	0.78	0.38
	1400	18.6	29.5	4.36	-10.67	0.47	0.57
	1500	18.9	30.2	1.87	-4.77	0.78	0.38
	1600	18.2	29.1	1.87	-4.57	0.79	0.38
	1700	18	28.7	1.56	0.49	0.94	0.76
	1800	17.3	25.1	0.63	4.14	1.27	0.19
	1900	16.4	18.6			3.09	0.39
	2000	15.7	15.9	0.33	-5.01	2.63	0.60
	Ave	14.92	23.52	6.24	-7.38	6.78	1.07
	Std Dev	3.51	6.70	5.54	7.75	10.56	0.78

Day	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
24-Mar-94 Corn 5	600	13.2	14.8	2.32	-11.09	89.06	0.40
	700	13.5	16.5	3.95	-8.37	96.90	0.40
	800	14.4	19.4	3.25	-6.48	58.60	0.98
	900	15.8	24.3	4.29	-3.72	21.71	2.71
	1000	16.7	27.9	2.70	-3.17	9.31	1.72
	1100	18.1	30.3	2.84	-1.41	0.94	0.95
	1200	18.7	28.1	0.94	-1.16	0.63	0.38
	1300	20	31.5	3.28	-3.50	0.94	1.13
	1400	20.7	32.2	1.57	-0.85	1.24	0.57
	1500	20.1	29.8	1.25	-0.11	0.94	0.57
	1600	20.3	27.5	1.25	-2.42	1.26	0.57
	1700	19.9	28.2	0.96	-1.27	1.58	0.76
	1800	19.4	25.6	0.97	-4.36	1.75	0.00
	1900	18.8	21.7	1.60	-5.86	3.87	0.59
	Ave	17.83	25.56	2.23	-3.84	20.62	0.84
	Std Dev	2.63	5.51	1.16	3.16	34.40	0.68

Hourly Averages, Standard Deviations

Winter/Spring NOx measurements, Central Crops Research Station, Clayton NC.

Air Carrier

N2 Carrier

Soybean data	Hour	Soil Temp	Air Temp	NO Flux	NO2 Flux	NO Flux	NO2 Flux
	600	2.10	0.00	-0.33	5.60	0.87	0.00
	600	2.70	5.00	3.57	7.58	2.39	0.41
	ave	2.40	2.50	1.62	6.59	1.63	0.21
	std dev	0.42	3.54	2.76	1.40	1.08	0.29
	700	1.20	0.50	5.88	-74.53	1.91	0.00
	700	2.00	0.20	22.42	4.44	1.74	0.00
	700	3.30	10.80	7.67	-22.63	5.02	1.22
	ave	2.17	3.83	11.99	-30.91	2.89	0.41
	std dev	1.06	6.04	9.08	40.13	1.85	0.70
	800	8.10	12.50	1.65	0.40	0.66	0.00
	800	1.50	1.90	75.90	-68.19	3.11	0.00
	800	2.10	2.50	21.27	-14.92	5.17	0.00
	800	4.80	15.60	6.58	-10.69	2.96	0.60
	ave	4.13	8.13	26.35	-23.35	2.98	0.15
	std dev	3.01	6.96	34.07	30.58	1.84	0.30
	900	9.10	13.10	3.95	-1.78	0.17	0.00
	900	0.90	5.00	26.52	-34.58	1.88	3.31
	900	2.00	4.30	39.55	-52.33	3.77	0.00
	900	2.80	6.90	8.29	-7.49	6.78	0.00
	900	6.30	14.30	6.94	-2.01	7.10	1.00
	ave	4.22	8.72	17.05	-19.64	3.94	0.86
	std dev	3.40	4.66	15.38	22.74	3.03	1.44
	1000	9.80	13.80	3.62	-2.51	0.00	0.00
	1000	1.70	6.00	28.53	-41.28	0.00	1.65
	1000	3.60	9.30	11.20	-6.59	18.83	0.00
	1000	7.50	16.50	5.53	0.58	11.31	0.99
	ave	5.80	11.35	12.22	-12.45	7.54	0.66
	std dev	3.60	4.63	11.34	19.44	9.23	0.81
	1100	10.20	12.30	2.31	-9.83	0.42	2.02
	1100	11.50	16.10	2.61	-2.31	0.33	0.00
	1100	4.00	8.10	6.71	-27.64	0.00	0.00
	1100	6.30	12.00	18.52	-28.38	0.67	0.00
	1100	6.00	12.20	7.60	-1.92	33.12	0.00
	1100	10.10	19.30	4.86	-5.32	27.12	1.77
	ave	8.02	13.33	7.10	-12.57	10.27	0.63
	std dev	2.98	3.87	5.98	12.29	15.49	0.98
	1200	12.50	13.80	13.15	-22.94	0.00	0.00
	1200	11.80	16.00	0.65	-2.73	0.82	0.00
	1200	6.30	9.00	8.69	-23.78	0.00	0.00
	1200	7.70	13.20	15.81	-27.18	5.80	0.00
	1200	8.70	13.70	4.27	-6.63	43.71	0.00
	1200	12.10	21.30	4.66	-8.22	31.29	1.76
	ave	9.85	14.50	7.87	-15.25	13.60	0.29
	std dev	2.62	4.04	5.78	10.53	19.04	0.72
	1300	14.20	15.20	8.18	-27.05	0.08	0.00
	1300	11.60	15.10	0.49	-3.24	1.48	0.00
	1300	8.00	10.50	7.65	-18.38	0.33	0.20
	1300	9.80	16.10	7.82	-16.64	7.06	0.00
	1300	10.50	15.00	5.26	-9.03	48.29	0.20
	1300	12.30	23.00	2.87	2.47	31.59	2.33
	ave	11.07	15.82	5.38	-11.98	14.81	0.46
	std dev	2.14	4.04	3.14	10.80	20.33	0.93

1400	14.20	15.20	-3.22	-14.45	0.20	0.00
1400	9.00	11.60	4.31	-23.97	0.33	0.20
1400	10.10	15.20	5.56	-13.52	4.61	0.00
1400	12.10	16.00	3.26	-6.60	52.23	0.00
1400	13.70	23.90	2.39		19.18	0.00
ave	11.82	16.38	2.46	-14.64	15.31	0.04
std dev	2.25	4.54	3.39	7.14	22.05	0.09
1500	14.10	15.70	3.92	-2.18	0.00	0.00
1500	9.20	12.20	2.97	-12.49	0.17	0.20
1500	10.00	15.60	3.27	-21.51	15.30	0.00
1500	12.80	17.60	1.62	-3.28	42.63	0.00
1500	14.10	23.60	2.08	-8.30	10.88	4.85
ave	12.04	16.94	2.77	-9.55	13.79	1.01
std dev	2.31	4.20	0.92	7.86	17.45	2.15
1600	12.50	16.30	2.28	7.74	0.00	0.00
1600	8.80	11.80	0.00	-23.66	0.00	0.00
1600	9.50	14.50	2.95	-19.94	16.01	0.00
1600	11.60	16.60	2.50		19.83	0.20
1600	13.80	23.90	1.29	-6.05	8.31	2.91
ave	11.24	16.62	1.80	-10.48	8.83	0.62
std dev	2.08	4.50	1.18	14.31	9.07	1.28
1700	11.00	15.00	0.00	-3.00	0.08	0.00
1700	8.10	11.10	1.00	-21.89	0.00	0.00
1700	9.30	13.80	1.31	-9.51	12.25	0.00
1700	11.00	14.30	62.25	-37.70	19.82	0.20
1700	13.10	23.70	0.95	-1.57	8.80	2.72
ave	10.50	15.58	13.10	-14.73	8.19	0.58
std dev	1.90	4.77	27.48	15.14	8.44	1.20
1800	10.10	11.60	0.00	10.67	0.00	0.00
1800	7.00	8.20	-4.21	-55.13	0.00	2.05
1800	8.50	10.60	1.00	-9.21	21.25	0.00
1800	9.50	11.40	3.21	27.60	12.85	0.20
1800	12.00	18.50	0.32	-4.83	8.30	1.58
ave	9.42	12.06	0.06	-6.18	8.48	0.77
std dev	1.86	3.85	2.70	30.95	9.03	0.97
1900	6.10	4.60	45.51	-88.63	0.00	0.00
1900	7.30	5.90	11.54	-33.90	22.46	0.00
1900	8.60	8.70	2.41	-30.96	9.27	0.20
1900	11.00	15.50	0.83	9.94	10.69	2.00
ave	8.25	8.68	15.07	-35.89	10.61	0.55
std dev	2.10	4.86	20.83	40.46	9.22	0.97
2000	5.50	3.50	133.06	-141.04	0.69	0.00
2000	6.50	4.50	-10.77	-37.21	18.47	0.00
2000	7.80	5.90	44.45	-41.45	6.13	0.41
2000	10.30	13.60	0.33	26.01	9.27	1.61
ave	7.53	6.88	41.77	-48.42	8.64	0.50
std dev	2.08	4.59	65.37	69.02	7.45	0.76
2100	9.60	12.00	0.51	-8.81	9.16	1.62
2200	9.20	11.30	2.34	1.58	7.51	2.02
2300	8.70	10.10	10.17	23.92	7.38	2.44
2400	8.40	10.00	40.99	38.45	7.38	5.49
2500	8.00	10.10	9.01	17.08	6.71	9.56
2600	7.70	10.20	0.69	4.53	6.03	4.47
2700	7.30	8.50	3.91	-0.33	5.90	2.25

2800	6.90	7.90	0.36	0.54	5.07	1.23
2900	6.70	7.00	0.85	-0.78	5.42	1.23

Cotton data	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
	600	3.80	4.00	-11.71	-53.30	1.03	0.42
	600	3.50	1.70	17.69	2.01	4.49	0.21
	600	13.20	13.60	1.01	-1.93	1.16	0.20
	600	6.20	6.30	2.36	-9.18	23.11	0.21
	ave	6.68	6.40	2.34	-15.60	7.45	0.26
	std dev	4.51	5.15	12.04	25.56	10.56	0.11
	700	3.90	3.20	4.14	-37.62	1.37	0.42
	700	3.40	1.80	7.80	-6.58	0.86	0.42
	700	7.80	8.20	109.55	-63.49	3.21	1.02
	700	13.30	14.70	2.29	6.38	4.62	0.40
	700	6.60	7.80	4.72	-6.65	42.43	0.41
	ave	7.00	7.14	25.70	-21.59	10.50	0.53
	std dev	3.97	5.07	46.92	28.47	17.91	0.27
	800	3.90	3.60	10.66	1.01	1.20	0.21
	800	3.30	2.10	19.72	-0.62	1.04	0.00
	800	8.30	10.20	19.24	-24.84	4.53	0.61
	800	13.70	16.70	5.55	-9.29	5.73	0.40
	800	6.90	8.40	4.89	-9.99	38.96	0.41
	ave	7.22	8.20	12.01	-8.75	10.29	0.32
	std dev	4.17	5.80	7.18	10.27	16.16	0.23
	900	4.00	3.00	5.04	-4.74	1.72	0.00
	900	4.00	3.30	14.95	-20.77	1.37	0.00
	900	9.90	14.10	18.45	-10.19	6.28	0.00
	900	14.80	20.10	3.73	-8.04	2.11	0.20
	900	7.50	10.00	4.00	-11.31	28.68	0.41
	ave	8.04	10.10	9.23	-11.01	8.03	0.12
	std dev	4.53	7.29	6.95	6.00	11.71	0.18
	1000	4.20	2.50	10.50	15.11	3.96	0.00
	1000	5.00	4.20	18.01	-23.75	1.20	0.00
	1000	13.20	21.20	6.90	-6.34	30.17	3.91
	1000	15.90	25.10	4.60	-6.81	7.01	0.97
	1000	9.20	16.10	7.85	-16.35	12.31	1.00
	ave	9.50	13.82	9.57	-7.63	10.93	1.17
	std dev	5.08	10.09	5.17	14.62	11.52	1.61
	1100	4.30	3.30	8.94	-3.54	3.95	0.00
	1100	5.00	4.60	14.20	-14.42	0.85	0.00
	1100	13.90	24.30	5.73	-6.84	39.27	2.32
	1100	16.30	27.80	3.16	-3.59	16.41	1.34
	1100	11.90	20.90	5.47	-3.23	2.75	0.39
	ave	10.28	16.18	7.50	-6.32	12.65	0.81
	std dev	5.38	11.44	4.27	4.76	16.09	1.01
	1200	4.80	3.80	3.43	-0.57	6.69	0.00
	1200	4.90	4.80	8.89	-11.10	0.85	0.00
	1200	17.70	28.20	4.43	-6.11	6.30	1.72
	1200	18.20	30.10	6.86	-4.04	6.58	1.33
	1200	13.00	22.70	3.06	-11.22	1.44	0.39
	ave	11.72	17.92	5.33	-6.61	4.37	0.69
	std dev	6.59	12.73	2.48	4.60	2.95	0.79



1300	5.00	4.20	3.24	-1.09	10.79	0.00
1300	5.00	5.40	8.54	-12.60	0.68	0.00
1300	18.00	26.20	2.57	-2.98	5.24	0.38
1300	20.10	31.50	2.33	-2.74	2.49	0.76
1300	11.00	14.50	4.44	-19.77	0.99	0.20
ave	11.82	16.36	4.22	-7.84	4.04	0.27
std dev	7.08	12.22	2.55	8.07	4.18	0.32
1400	5.10	4.10	1.57	-5.28	17.81	0.21
1400	5.60	6.60	5.47	-7.78	1.53	0.00
1400	17.60	27.60	1.88	-2.96	2.68	0.00
1400	21.00	31.20	1.26	-1.27	1.72	0.57
1400	11.80	20.40	4.67	0.07	0.81	0.20
ave	12.22	17.98	2.97	-3.44	4.91	0.19
std dev	7.08	12.20	1.95	3.14	7.24	0.23
1500	5.00	3.70	1.39	0.99	10.64	0.21
1500	6.70	7.10	2.92	-12.70	0.85	0.00
1500	17.80	26.80	1.11	-2.40	2.85	0.00
1500	20.10	28.30	0.94	-0.78	1.42	0.19
1500	12.60	18.60	2.26	-0.45	0.65	0.20
ave	12.44	16.90	1.72	-3.07	3.28	0.12
std dev	6.63	11.19	0.84	5.52	4.20	0.11
1600	5.00	3.50	2.73	-1.40	19.05	0.00
1600	6.30	7.80	2.19	-4.65	0.85	0.00
1600	17.80	27.80	1.42	-9.55	3.63	0.00
1600	18.80	28.00	1.57	-2.86	1.10	0.00
1600	13.20	19.70	2.60	-3.63	0.65	0.39
ave	12.22	17.36	2.10	-4.42	5.06	0.08
std dev	6.38	11.30	0.59	3.10	7.92	0.18
1700	4.70	3.10	1.02	0.22	15.13	0.00
1700	6.20	8.10	1.19	1.07	0.34	0.00
1700	17.30	27.00	1.26	-3.05	4.43	0.00
1700	18.20	27.00	0.94	-2.68	2.06	0.00
1700	13.20	20.20	0.05	-4.01	0.49	0.20
ave	11.92	17.08	0.89	-1.69	4.49	0.04
std dev	6.22	10.98	0.49	2.20	6.17	0.09
1800	4.50	3.50	0.52	1.25	12.53	
1800	5.80	7.20	-0.11	0.14	2.20	0.21
1800	16.30	22.00	1.60	-0.84	7.08	0.00
1800	17.60	23.60	0.66	-6.18	4.64	0.19
1800	12.50	16.60	-0.30	-23.16	0.49	0.89
ave	11.34	14.58	0.47	-5.76	5.39	0.35
std dev	5.97	8.91	0.75	10.14	4.71	0.44
1900	4.30	3.20	0.52	2.91	12.03	0.00
1900	5.20	6.30	0.70	3.10	4.25	2.06
1900	15.20	18.70	0.65	-1.56	8.95	0.00
1900	16.60	20.30	0.00	4.38	2.91	0.20
1900	12.00	16.00	0.35	3.37	0.66	0.40
ave	10.66	12.90	0.44	2.44	5.76	0.53
std dev	5.65	7.68	0.28	2.31	4.63	0.87
2000	4.10	3.00	3.10	2.72	11.69	0.00
2000	5.00	6.70	0.70	11.65	5.60	0.21
2000	14.80	17.40	0.17	1.87	8.99	0.00
2000	16.10	19.80	0.52	0.03	2.92	0.20

2000	11.30	11.70	0.33	-15.79	0.67	2.22
ave	10.26	11.72	0.96	0.10	5.97	0.53
std dev	5.51	7.05	1.21	9.95	4.46	0.95
2100	4.60	6.10	0.72	2.87	5.61	0.00
2100	10.50	9.70	1.51	-11.55	1.18	2.24
ave	7.55	7.90	1.12	-4.34	3.39	1.12
std dev	4.17	2.55	0.56	10.20	3.14	1.58
2200	4.30	6.00	1.04	1.41	5.44	0.21
2200	9.70	9.80	0.36	-5.82	1.01	0.20
ave	7.00	7.90	0.70	-2.20	3.23	0.20
std dev	3.82	2.69	0.48	5.11	3.14	0.00
2300	9.20	11.60	-0.31	1.14	1.00	0.61
2400	9.00	12.00	1.02	-1.67	0.83	0.00
2500	8.80	11.60	0.51	-1.29	1.50	0.00
2600	8.70	10.90	0.69	-1.62	0.84	0.00
2700	8.90	10.80	-0.28	-0.95	1.17	0.20
2800	8.50	10.00	0.02	-0.64	1.17	0.20
2900	8.20	8.80	0.23	0.99	0.67	0.20

Corn data	Hour	Soil Temp	Air Temp	Air Carrier		N2 Carrier	
				NO Flux	NO2 Flux	NO Flux	NO2 Flux
	600	8.00	7.10	0.34	-10.25	1.19	0.41
	600	3.30	0.00	2.26	-3.46	17.56	1.90
	600	10.60	11.70	1.83	-8.49	23.34	3.44
	600	9.30	7.80	17.03	-3.58	24.85	2.46
	600	13.20	14.80	2.32	-11.09	89.06	0.40
	ave	8.88	8.28	4.76	-7.37	31.20	1.72
	std dev	3.66	5.58	6.91	3.64	33.68	1.32
	700	8.10	11.50	5.81	-12.52	14.35	0.00
	700	3.70	5.00	6.70	-15.52	24.07	0.21
	700	10.80	12.60	3.30	-7.13	32.57	1.01
	700	9.70	16.00	14.40	-7.50	36.79	2.19
	700	13.50	16.50	3.95	-8.37	96.90	0.40
	ave	9.16	12.32	6.83	-10.21	40.94	0.76
	std dev	3.63	4.62	4.45	3.67	32.44	0.88
	800	8.30	10.80	4.50	-12.38	19.90	0.20
	800	4.30	10.20	10.19	-10.39	20.28	0.20
	800	11.50	14.20	8.53	-11.06	37.68	1.00
	800	10.60	20.00	10.62	-14.98	12.47	1.96
	800	14.40	19.40	3.25	-6.48	58.60	0.98
	ave	9.82	14.92	7.42	-11.06	29.79	0.87
	std dev	3.78	4.63	3.36	3.10	18.58	0.73
	900	9.00	13.30	3.82	-10.08	9.78	0.20
	900	4.70	10.00	10.66	-10.67	15.77	0.41
	900	13.00	18.60	8.90	-13.34	25.23	0.79
	900	11.30	22.30	13.30	-28.70	7.88	1.95
	900	15.80	24.30	4.29	-3.72	21.71	2.71
	ave	10.76	17.70	8.19	-13.30	16.07	1.21
	std dev	4.20	6.00	4.09	9.30	7.46	1.08
	1000	10.40	16.60	3.28	-5.30	0.98	0.20
	1000	6.80	13.20	5.45	-7.41	6.80	0.60
	1000	14.70	19.80	6.29	-4.48	12.00	1.57

1000	11.80	23.20	8.30	-9.52	5.93	1.75
1000	16.70	27.90	2.70	-3.17	9.31	1.72
ave	12.08	20.14	5.20	-5.98	7.00	1.17
std dev	3.84	5.71	2.28	2.51	4.11	0.72
1100	13.00	18.70	40.39	6.14	0.49	0.20
1100	8.30	13.00	4.18	-7.84	3.82	0.60
1100	16.20	22.40	4.00	-3.21	1.93	0.58
1100	13.40	27.20	4.71	-9.78	2.06	1.15
1100	18.10	30.30	2.84	-1.41	0.94	0.95
ave	13.80	22.32	11.22	-3.22	1.85	0.70
std dev	3.72	6.85	16.32	6.23	1.28	0.37
1200	13.60	16.20	3.26	-7.48	0.66	0.20
1200	11.20	15.50	5.23	-8.13	0.82	0.40
1200	16.80	23.70	3.35	-2.06	1.44	0.39
1200	16.80	29.50	5.30	-3.72	0.94	0.95
1200	18.70	28.10	0.94	-1.16	0.63	0.38
ave	15.42	22.60	3.61	-4.51	0.90	0.46
std dev	2.99	6.53	1.79	3.15	0.33	0.28
1300	13.20	18.70	3.55	-6.17	0.16	0.20
1300	12.30	18.30	4.30	-49.98	0.65	0.20
1300	17.50	26.60	4.89	-7.90	0.95	0.38
1300	17.80	29.70	3.11	-5.16	0.78	0.38
1300	20.00	31.50	3.28	-3.50	0.94	1.13
ave	16.16	24.96	3.83	-14.54	0.70	0.46
std dev	3.27	6.15	0.75	19.87	0.32	0.39
1400	14.70	17.70	2.59	-6.35	0.16	0.20
1400	12.70	18.70	6.83	-19.04	0.81	0.20
1400	17.60	25.10	3.48	-4.22	0.96	0.39
1400	18.60	29.50	4.36	-10.67	0.47	0.57
1400	20.70	32.20	1.57	-0.85	1.24	0.57
ave	16.86	24.64	3.77	-8.23	0.73	0.38
std dev	3.17	6.41	2.00	7.02	0.42	0.19
1500	14.10	21.30	1.62	-4.82	0.48	0.00
1500	12.70	18.70	3.55	-2.11	0.65	0.20
1500	17.00	25.60	3.16	-8.13	0.64	0.58
1500	18.90	30.20	1.87	-4.77	0.78	0.38
1500	20.10	29.80	1.25	-0.11	0.94	0.57
ave	16.56	25.12	2.29	-3.99	0.70	0.35
std dev	3.13	5.09	1.01	3.04	0.17	0.25
1600	13.60	21.20	1.60	-5.10	0.48	0.20
1600	12.00	18.00	7.45	7.85	2.61	0.40
1600	15.30	23.80	2.73	-1.67	0.80	0.39
1600	18.20	29.10	1.87	-4.57	0.79	0.38
1600	20.30	27.50	1.25	-2.42	1.26	0.57
ave	15.88	23.92	2.98	-1.18	1.19	0.39
std dev	3.37	4.53	2.56	5.25	0.84	0.13
1700	12.10	20.10	0.64	-18.58	1.30	0.00
1700	10.90	17.70	1.95	-9.55	0.65	0.20
1700	14.60	23.30	1.59	-8.58	1.28	0.19
1700	18.00	28.70	1.56	0.49	0.94	0.76
1700	19.90	28.20	0.96	-1.27	1.58	0.76
ave	15.10	23.60	1.34	-7.50	1.15	0.38
std dev	3.82	4.86	0.53	7.60	0.36	0.36

1800	10.00	11.50	0.00	-9.28	3.34	0.00
1800	9.60	10.80	1.33	-11.57	0.84	0.20
1800	13.70	20.00	1.93	-9.13	1.46	0.39
1800	17.30	25.10	0.63	4.14	1.27	0.19
1800	19.40	25.60	0.97	-4.36	1.75	0.00
ave	14.00	18.60	0.97	-6.04	1.73	0.16
std dev	4.34	7.15	0.73	6.27	0.96	0.16
1900	9.10	7.50	-0.16	-7.56	1.02	0.00
1900	8.70	6.40	3.26	-7.22	1.02	0.41
1900	12.80	14.50	5.61	25.33	2.48	1.20
1900	16.40	18.60			3.09	0.39
1900	18.80	21.70	1.60	-5.86	3.87	0.59
ave	13.16	13.74	2.58	1.17	2.29	0.52
std dev	4.44	6.72	2.46	16.12	1.26	0.44
2000	8.50	6.10	-0.31	-5.82	0.51	0.00
2000	8.10	4.00	3.95	-29.20	1.03	0.21
2000	12.00	12.40	-8.53	-7.52	2.33	2.62
2000	15.70	15.90	0.33	-5.01	2.63	0.60
ave	11.08	9.60	-1.14	-11.89	1.62	0.86
std dev	3.55	5.51	5.27	11.59	1.02	1.20
2100	7.60	4.70	-0.16	-4.36	0.68	0.00
2200	7.00	3.80	0.00	-4.12	0.34	0.00
2300	6.20	2.30	0.34	-3.86	0.17	0.21
2400	5.80	0.90	0.00	-3.47	0.00	0.00
2500	5.50	-0.30	0.00	-44.27	0.17	0.21
2600	5.20	-1.20	-17.51	-64.55	0.00	0.42
2700	5.10	-0.40	0.35	-4.99	0.17	0.21
2800	4.50	-1.50	1.04	-3.62	0.17	0.42
2900	4.10	-1.20	0.00	-1.01	0.17	0.21



# North Carolina State University

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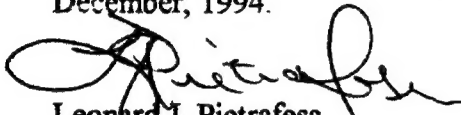
10 Aug 94

**To: AFIT/CIR**

**From: Department of Marine, Earth and Atmospheric Sciences (MEAS)**

**Subject: Completion of Master of Science Degree Requirements**

I hereby certify that Capt Benny D. Holbrook, [REDACTED] has completed all requirements for the MS degree in Atmospheric Science, and will receive this degree on 21 December, 1994.

  
Leonard J. Pietrafesa  
Department Head, MEAS

# REQUEST AND AUTHORIZATION FOR CHANGE OF ADMINISTRATIVE ORDERS

(If more space is required, use reverse, identifying items by number)

<b>TO:</b> 4 MSSQ/MSM 1215 MARTIN ST SEYMOUR JOHNSON AFB NC 27531			<b>FROM:</b> 4 MSSQ/MSMR 1215 MARTIN ST. ROOM 11 SEYMOUR JOHNSON AFB NC 27531			<b>TELEPHONE</b>  6807		
THE FOLLOWING ORDER IS: <input checked="" type="checkbox"/> AMENDED AS SHOWN IN ITEM 5( <input type="checkbox"/> Rescinded <input type="checkbox"/> Revoked <input type="checkbox"/> Totally <input checked="" type="checkbox"/> In Part)								
IDENTIFICATION OF ORDER BEING CHANGED (Issued by this Headquarters unless otherwise stated in item 6.)								
1. BASIC ORDER						2. PREVIOUSLY AMENDED BY		
A. PARA	B. ORDER (Type and Number)	C. DATE	D. <b>TED SEP94</b> <input checked="" type="checkbox"/> PCS WITH PCA (EDCSA) <input type="checkbox"/> PCS WITHOUT PCA			A. PARA	B. ORDER (Type and Number)	C. DATE
	80 A-800	29 JUN94						
3. RELATING TO (TDY, PCS, Short Tour of AD, etc.) <b>AAN: 0940NL2478 CAFSC: 015W1 RNLTD: 30SEP94</b> <b>334 TECHNICAL TRAINING SQ (AETC) KESSLER AFB MS 39534-5000</b>								
4. IDENTIFICATION OF INDIVIDUALS TO WHOM CHANGE ACTION PERTAINS								
A. GRADE	B. LAST NAME, FIRST, MIDDLE INITIAL		C. SSAN OR CIVILIAN POSITION TITLE			D. ORGANIZATION		
CPT	HOLBROOK BENNY D					AF INST OF TECH		
5. AMENDMENT (Identify item in order being amended)								
A. ITEM	AS READS				IS AMENDED TO READ			
B. ITEM	IS AMENDED TO (Include) (Delete) <b>24 AFIT START DATE: 5 AUG 92 AFIT STOP DATE: 15 AUG 94.</b>							
6. REMARKS <b>ORDERS AMENDED TO INCLUDE AFIT START/STOP DATE.</b>								
7. ACCOUNTING CITATION <b>5743500 324 5752.0* 503725 ATAC: F47B20*</b> <span style="border: 1px solid black; border-radius: 50%; padding: 2px;">dyf</span> <b>NTSC: 5743500 324 5758.0N 503725</b>								
8. DATE	9. ISSUING/APPROVING OFFICIAL (Typed name, grade, and title)				10. SIGNATURE			
5AUG94	<b>DAVID J. FISHMAN, TSGT, USAF</b> <b>PERSONNEL RELOCATIONS MANAGER</b>							
11. DESIGNATION AND LOCATION OF HEADQUARTERS					12. ORDER (Type and Number)		13. DATE	
<b>DEPARTMENT OF THE AIR FORCE</b> <b>4TH MISSION SUPPORT SQUADRON (ACC)</b> <b>1215 MARTIN ST. ROOM 11</b> <b>SEYMOUR JOHNSON AFB NC 27531</b>					SO A-959		5AUG94	
					14. TDN  <b>FOR THE COMMANDER</b>			
15. DISTRIBUTION					16. SIGNATURE ELEMENT OF ORDERS AUTHENTICATION OFFICIAL			
<b>"A"</b>  <b>GAINING MPF: 81 MSSQ/MSMR</b> <b>KESSLER AFB MS 39534</b>					  <b>DONNELL E. ADAMS, CAPTAIN, USAF</b> <b>CHIEF, MILITARY PERSONNEL FLIGHT</b>			

# REQUEST AND AUTHORIZATION FOR PERMANENT CHANGE OF STATION - MILITARY

(THIS FORM IS SUBJECT TO THE PRIVACY ACT OF 1974 - USE BLANKET PAS - AF FORM 11)

The following individual will proceed on permanent change of station: ☐ PCS without PCA ☒ PCS with PCA TED: SEP 94

1. GRADE, NAME (Last, First, Middle Initial) <b>CPT HOLBROOK BENNY D</b>	2. SSN [REDACTED]	3. SAFSC/CAFSC <b>015W1</b>
4. SECURITY CLEARANCE (Include date of last investigation) [REDACTED]	5. REPORT TO COMDR. NEW ASSIGNMENT. NLT <b>940930</b>	6. TRAVEL DAYS AUTHORIZED IF TRAVELING BY PRIVATELY OWNED CONVEYANCE <b>3</b>

7. TDY ENROUTE  
**3200 16 Shore Rd  
Raleigh NC 27631-5065**

8. UNIT, MAJOR COMMAND AND ADDRESS OF UNIT TO WHICH ASSIGNED <b>334 TECHNICAL TRAINING SQ (AETC KESSLER AFB MS 39534-5000</b>	9. UNIT, MAJOR COMMAND AND ADDRESS OF UNIT FROM WHICH RELIEVED <b>AF INST OF TECH IN OL SM04 RALEIGH CTY NC 27607</b>
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10. TYPE OF TOUR <input type="checkbox"/> ACCOMPANIED <input type="checkbox"/> UNACCOMPANIED <input type="checkbox"/> UNACCOMPANIED, DEPENDENTS RESTRICTED	11. TOUR LENGTH (TOTAL NO. OF MONTHS)	12. <input type="checkbox"/> EXTENDED LONG TOUR VOL
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13. DEPENDENT TRAVEL A. <input type="checkbox"/> CONCURRENT TRAVEL IS AUTOMATIC B. <input type="checkbox"/> CONCURRENT TRAVEL IS APPROVED C. <input type="checkbox"/> NONCONCURRENT TRAVEL IS AUTHORIZED IN LESS THAN 20 WEEKS D. <input type="checkbox"/> NONCONCURRENT TRAVEL IS AUTHORIZED IN MORE THAN 20 WEEKS E. <input type="checkbox"/> TRAVEL IS AUTHORIZED TO A DESIGNATED PLACE	14. <input type="checkbox"/> THIS IS A JOIN-SPOUSE ASSIGNMENT (INCLUDE SPOUSE'S NAME, SSN, AND PAY GRADE)
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15. AUTHORITY FOR CCTVL	16. HOMEBASING/FOLLOW-ON ASSIGNMENT (INCLUDE AAN, GPAS, AND RNLT D)
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17. DEPENDENT(S): (LIST NAMES, DOB OF CHILDREN, RELATIONSHIP TO MEMBER AND CURRENT ADDRESS)	18. DEPARTURE CERTIFICATION: I certify that to the best of my knowledge I will depart PCS at _____ (hrs) _____ (date).  (Signature)
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19. OVERSEAS TRANSPORTATION DATA:  
☐ A. Comply with MTA (DD Form 1482)  
☐ B. Member will comply with reporting time and flight reservations in the MTA or as arranged by the TMO per AFR 75-8, and is not authorized to depart this station before receipt of validated MTA or GTR (SF1169) from the TMO.  
☐ C. TDY station will obtain flight reservations. Member is not authorized to depart TDY station before receipt of validated MTA or GTR (SF1169) from the TMO.  
☐ D. Dependent(s) will comply with reporting data and flight reservations in the MTA.

20. PCS EXPENSE CHARGEABLE TO <b>5743500 324 5752.0*503725</b> CIC: <b>NONTEMPORARY STORAGE CHARGEABLE TO 5743500 324 5758.0N 503725</b>	(Insert M.D.H.I.G.F.A.S.C.T. or Y) TAC: ATAC: <b>F47B20*</b>	21. AUTHORITY AND PCS CODE AFR 36-20, PCS ID: <b>C</b> AAN: <b>0940NL2478</b>
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22. TDY EXPENSE CHARGEABLE TO	23. EXCESS BAGGAGE AUTHORIZATION  PIECES LBS
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Pursuant to AFR 90-1, you will report to the base housing referral office servicing your new duty station before entering any rental, lease, or purchase agreement for off-base housing.

24. REMARKS (Submit travel voucher within 5 workdays after completion of travel. If TDY enroute is authorized, attach receipts showing cost of all lodgings used. All promotional items incurred while PCS/TDY must be turned in to AFO upon arrival at gaining base.)  
**ITEMS 1, 2, 13 AND 15 ON REVERSE APPLY.**

25. DATE <b>28JUN94</b>	26. CBPO OFFICIAL (Type Name and Grade) <b>DAVID J. FISMAN, TSGT. USAF PERSONNEL RELOCATIONS MANAGER</b>	27. SIGNATURE OF CBPO OFFICIAL 
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28. DESIGNATION AND LOCATION OF HEADQUARTERS DEPARTMENT OF THE AIR FORCE <b>4 MISSION SUPPORT SQ (ACC) SEYMOUR JOHNSON AFB NC 27531</b>	29. SPECIAL ORDER NO. <b>A-800</b>	30. DATE <b>29JUN94</b>
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32. DISTRIBUTION <b>A</b>	33. SIGNATURE ELEMENT OF ORDERS AUTHENTICATING OFFICIAL   <b>DONNELL E. WILLIAMS, MS, CAPT, USAF CHIEF, MILITARY PERSONNEL</b>
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REFERENCE ITEM 24 - ONLY ITEMS ON THE REVERSE THAT ARE INDICATED APPLY:

1. Thirty days prior to your Projected Departure Date, report to Outbound Assignments. Bldg 4700 RM 7 to schedule your final outprocessing appointment. Failure to comply could result in delaying your outprocessing and departure.
2. Contact Military Pay, Accounting and Finance when you are within 10 days of your Projected Departure Date to begin outprocessing actions.
3. Report to DND MTS 3 days prior to your final outprocessing date to obtain your Military Transportation Authorization (MTA).
4. Member is authorized 4 days proceed time. (Unaccompanied overseas only)
5. Early reporting is authorized at the discretion of the Unit Commander.
6. This assignment is as: (a) Humanitarian; (b) Special Duty Assignment; (c) ETO; (d) CONUS Exchange; (e) Permissive; (f) VERAP; (g) VECAP.
7. Member has an approved Home-Basing Agreement and has agreed not to relocate dependents, ship POV, move or store household goods, at government expense or personal expense.
8. Member has an approved Follow-On Agreement and has agreed not to relocate dependents, ship POV, move or store household goods, at government expense or personal expense, except to the Follow-On location.
9. La persona a quien esta orden pertenece esta autorizada por las autoridades militares competentes de los Estados Unidos de America para entrar o salir de Espana en mision oficial vestida de civil o militar.
10. Concurrent travel of dependents was authorized up to 4 months beyond sponsor's report no later than month.
11. Assignment to a remote station in Alaska. Dependents are not authorized. Aircrews are allowed 2 pieces of checked baggage and 1 piece of carry-on luggage enroute to Elmendorf AFB (EAFB). Total weight allowance of checked baggage must not exceed 160 lbs. On arrival at EAFB an additional piece of checked baggage will be authorized for issuance of military arctic gear. Total checked baggage from EAFB to remote site must not exceed 210 lbs. AFSCs 31111, 42111, 44111, and 90210 are authorized 15 days TDY enroute and all other AFSCs are authorized 5 days TDY enroute to EAFB for processing and transportation to the final destination. Shipment of POV is not authorized. Member must hold a valid government drivers license and be small arms qualified prior to arrival. Report to 3 HHSQ/HSPOM, EAFB MTS the first duty day after arrival.
12. Member authorized POV travel via Alaska Highway including Alaska Marine Highway System.
13. Change in marital status should be reported to Outbound Assignments ASAP.
14. Member authorized full JFTN weight allowance for electing the Accompanied by Dependents tour.
15. Member authorized 8 days Permissive TDY for the purpose of house hunting. Member should report to the Base Housing Office before entering into any rental, lease or purchase agreements for off base housing.
16. Member authorized 2000 lbs or 75% of Full JFTN weight allowance whichever is greater.
17. Member authorized to use 3 privately owned conveyances in conjunction with this move. Determination of special authorization maintained in 6 HHSQ/HSPOM.

18. NATO TRAVEL ORDER/ORDRE DE MISSION OTAN

Country of Origin: United States Order Number: SEE ITEM 29  
 Pays de provenance: \_\_\_\_\_ Numero de series: SEE ITEM 29  
 1. The bearer (and group as shown herein or attached list) La porteur (et personnel porte ci-dessus ou sur la liste jointe)  
SEE ITEM 1 and ITEM 2 for bearer and ITEM 17 for group if applicable.  
 2. WILL TRAVEL FROM SEE ITEM 9 to SEE ITEM 8  
 VERA MOUVEMENT DE SEE ITEM 9 to SEE ITEM 8  
 via \_\_\_\_\_ Date of departure SEE ITEM 3  
 via \_\_\_\_\_ Date de depart SEE ITEM 3  
 3. Authority is not granted to possess and carry firearms.  
 Autorisation de port d'armes non accordée.  
 4. The person named in paragraph 1 is authorized to carry SEE ITEM 24  
 La personne indiquée au paragraphe 1 est autorisée a porte sealed dispatches  
SEE ITEM 24  
 plus scellées, ne contenant que des documents officiels, numerotes  
 5. I hereby certify that this individual/group is/are member(s) of a force  
 as defined in the NATO Status of Forces Agreement, and that this is an authorized  
 move under the terms of this agreement.

Je soussigne certifie que le personnel vise appartient a une armee telle que definir  
 dans l'Accord OTAN sur le status des Forces armees et que ce deplacement est officiel  
 selon les termes de ce Accord.

6. This travel order is to be produced to civil and military authorities on request  
 Cet ordre de mission devra etre presente sur demande autorites civiles et militaires.

FOR THE COMMANDER

SEE ITEM 23  
 Officer authorizing movement  
 Official autorisant le mouvement

SEE ITEM 30  
 Date of issue  
 Date de l'autorisation